# ALMA MATER STUDIORUM
# UNIVERSITÀ DI BOLOGNA

## SCUOLA DI SCIENZE

Corso di laurea magistrale in
*Environmental assessment and management, curriculum Climate KIC*

Titolo della tesi
# Biochar as a filter material: feasibility studies and business development

Tesi di laurea in
Sistemi di gestione ambientale, di politica ed economia ambientale

Relatore
Prof. Andrea Contin

Presentata da
Carlotta Carlini

Correlatori
Diego Marazza
Nicolas Greggio

Sessione unica

Anno accademico 2018/2019

# ABSTRACT

The goal of the thesis is to evaluate the performance of the biochar produced by a novel pyrolysis-with-post-reforming technique (TCR), as a filtering material for wastewater, and to make a comparison with other filter materials currently on the market. Caviro winery was chosen as a case study, providing two samples of wastewater produced in their plants. Vineyard pruning was used as the feedstock for the production of biochar.

Two different types of biochar were produced, which differ in the temperature at which the post-reformer was set during production (500°C and 700°C). For the two biochars and the two wastewater samples several analyses were conducted, aimed at their chemical and physical characterization.

Biochar and wastewater samples have been used for sorption tests of COD and other elements contained in the wastewater, with contact times of 0.5, 2, 6, and 24 hours. The resulting waters were then re-characterized. The performance of the two biochars as filtering materials were compared with materials currently marketed for this purpose, like active carbon and commercial zeolite.

An economic analysis has been performed which shows that the filtering of wastewaters with the biochar produced at the highest temperature is much less expensive than the current filtering materials and also with respect to the cost of standard processing by waste management companies in the Emilia-Romagna region (Italy).

# Table of Contents

# ACRONIMS

| | |
|---|---|
| BET | Brunauer, Emmett and Teller method |
| COD | Chemical Oxygen Demand |
| EPA | Environmental Protection Agency |
| GWP | Global Warming Potential |
| HTC | Hydrothermal Carbonization |
| IBI | International Biochar Initiative |
| SSA | Specific Surface Area |
| TCR | Thermo-Chemical Reforming |
| TSS | Total Suspended Solid |

# 1 INTRODUCTION

## 1.1 Motivation

Over the next two decades, the global population and the corresponding water consumption should increase rapidly. The United Nations estimates that in 2050 the world population will be 9.1 billion people.[1] According to the Organisation for Economic Co-operation and Development (OECD), the demand for water is going to increase by 55% by 2050.[2]

The water necessary for living does not consist only of drinking and sanitary water, but also of the one for cultivation of vegetables, for animal breeding, for the production and processing of beverages and packaged foods. Uses of water are many and diversified. Therefor it is necessary to identify new ways to purify used waters and new materials that can be used in water purification with lower costs, but equal or better performance than those currently used.

Biochar is a carbonaceous material that is produced by the thermo-chemical conversion of different types of biomass in absence of oxygen. This material has been known as a soil improver for hundreds of years. More recently it has also been rediscovered for its properties of absorbing pollutants. It has been noted that when in contact with aqueous solutions it is able to remove various substances such as heavy metals, organic material, inorganic elements.

This versatility makes it an extremely interesting product, because it can be applied in different fields. Furthermore, a wide variety of materials can be used for its production, including, in particular, wastes or residues which can be valorised in a circular economy poit of view.

## 1.2 Thesis goal

The purpose of the work described in this thesis was to test the performance of biochar produced through the Thermo-Chemical Reforming process as a filter material for

---

[1] https://www.dw.com/en/world-population-to-reach-97-billion-by-2050-un/a-49241728

[2] https://www.oecd.org/water/water-quantity-and-quality.htm

wastewater provided by an Italian winery, specifically the sorption of organic matter and ions present in the wastewater.

The wastewaters used in the experiments described in the thesis were provided by an Italian winery, and the biochar was produced from prunings produced within the wine supply chain. In this way we have tried to examine circularity within the supply chain, to exploit waste and to close material cycles.

The final outcome is to put the knowledge on biochar as a filtering material into practice, through experiments that simulate real conditions, using real wastewater and producing biochar from a feedstock that is readily available to the winery.

## 1.3 Definitions

### 1.3.1 Biochar

Charcoal is the black carbon residue produced by removing water and other volatile constituents from animal and plant materials. Charcoal is usually produced by heating of wood or other organic materials in the absence of oxygen, and used mainly as a fuel for heat and steel production.

Biochar is a carbonaceous material, similar to charcoal, and defined by The International Biochar Initiative (IBI) as ‘‘a solid material obtained from the thermo-chemical conversion of biomass in an oxygen-limited environment’’ (IBI, 2012).

Biochar origin is located in ancient south America, Amazonian Region, where it was known as Terra Petra, and it was used as soil amendment because of its fertilising properties (Ahmad et al., 2014). For these same reasons, biochar has recently attracted the interest of scientist. Terra Petra consists mainly of charcoal, pottery, bones and other wastes and soils and it shows higher amounts of nitrogen, phosphorus and potassium than adjacent soils (Shackley, Ruysschaert, & Glaser, 2016).

Biochar can be produced via different processes, like pyrolysis, gasification and HydroThermal Carbonization (HTC). Pyrolysis itself can be operated in different ways, modifying the process parameters, the most important being the temperature and residence time. There are different types of pyrolysis: fast, intermediate and slow.

Biochar characteristics are strongly related to the parameters of the process through which it has been produced. This leads to a wide range of biochars with different properties. The starting feedstock also plays a fundamental role in determining the future characteristics of biochar.

Among the different properties of biochar there are some that must be (or is highly desirable to be) characterized. These are carbon (C) content, as well as hydrogen (H), oxygen (O), nitrogen (N), surface area and porosity. However, a common regulation about biochar does not exist among countries, therefore the properties to be characterized may be more or be different from those listed above.

These properties are directly linked to the benefits that the biochar can bring to the soil, if used as a soil amendant, and to its performances as, e.g., filter material. These benefits and performances are: increase in crop yields, in nutrients and water availability, sorption of pollutants from both soil and aqueous solutions and carbon capture and storage (Shackley et al., 2016).

Biochar presents a large number of pores in its structure, and that reflects on its surface area. Since some of the pores are closed inside the structure, not open to the outside and, therefore, useless from an applicative point of view, it is important to know how much surface of the pores is connected to the outside. This quantity is referred as Specific Surface Area (SSA). SSA in reported in $m^2/g$ and measured through the Brunauer, Emmett and Teller (BET) method (Fagerlund, 1973). BET measures surface area based on gas adsorption. It has been observed that BET area tends to increase with increasing pyrolytic temperature. This happens due to the emission of the volatile substances during the pyrolysis process (Tan et al., 2015).

The surface area is generally negatively charged and, consequently, tends to attract positively charged ions and molecules, such as $Na^+$, $Ca^{2+}$, $K^+$, $NH_4^+$. These property to sorb cations is known as cation exchange capacity (Shackley et al., 2016).

### 1.3.2 Feedstock characteristics

Feedstock properties and play an important role in the characteristics of the pyrolysis products. For example, pyrolysis systems normally tolerate a moisture content in the feedstock of up to 30 wt%. A higher moisture content would lead to a greater energy consumption, due to the need to remove excess water by evaporation (Hornung, 2014; Shackley et al., 2016).

Feedstock size, shape, density and uniformity are other important characteristics that can have an influence in the pyrolysis process and affect the resulting products. It must be suitable for the chosen technology, in order to prevent partially un-pyrolyzed material.

The feedstock can be identified based on its size. The principal size classes for feedstock are shown in Table 1.

Table 1 - Feedstock size classes (Sluiter, Ruiz, Scarlata, Sluiter, & Templeton, 2010)

| **Classes** | **Size** |
|---|---|
| Cordwood or firewood | From 10 to 100 cm |
| Chipped and shredded | From 2 mm to several cm |
| Pelletized | Diameter: 0,5-1 cm<br>Length: several cm |
| Sawdust-like fine particles | Less than 2 mm |

Unlike fast pyrolysis, which requires fine powders to allow for fast heat transfer, intermediate pyrolysis particles of up to 50 mm can be used (Schmitt et al., 2019).

A wide range of organic materials can be exploited for biochar production. Three categories can be defined: a) first choice feedstock, such as dedicated crops and wood; b) residual biomass, such as bagasse, wood waste, agricultural wastes and prunings; and c) wastes like sewage sludge, municipal waste, food processing waste and animal manure.

Although all these feedstocks are suitable to produce biochar, the first category presents problems, in particular related to competition with food. In fact, dedicated crops and wood cultivation would require the use of soil for non-food purposes.

Residual biomass and waste management represent nowadays a challenge all over world. For these reasons, residual biomasses and waste are better options, avoiding food competitions and contributing to waste management.

However, wastes present problems, mainly related to the possible presence of contaminants. Other problems are the continuous availability over time and the possible decentralization of the material. The availability of wastes in specific places depends exclusively on the way in which they are produced, collected and managed.

As regards to the presence of contaminants, the greatest danger is represented by heavy metals, fertilizers residues and the accidental addition of other materials during the collection and transport phases. This can lead to the presence of unwanted elements and molecules, and it may contribute to the increase in ash content.

Ash content is a property of biochar that needs to be characterized. Ash is the most nutrient-rich part of the biochar, and it is therefore important when biochar is applied to soil, but it can also be a problem if the goal is to exploit the sorbent properties of biochar, because ashes can occlude the pores thus decreasing the specific surface (Hornung, 2014; Shackley et al., 2016).

### 1.3.3 Biochar production technologies

Among the different technologies to produce biochar, some of them where specifically developed for this purpose, others get biochar as a secondary product. This leads to very different biochar yields throughout the technologies, which are summarized in the following.

1) **Pyrolysis**. Pyrolysis is a thermal conversion process that converts biomass in three different products, showed in Figure 1. The pyrolysis products consist in a solid phase, a liquid phase and a gas phase. The liquid phase is in turn composed of an aqueous phase and an oil phase. These products are generally known as biochar, bio-oil (plus process water) and syngas, respectively.

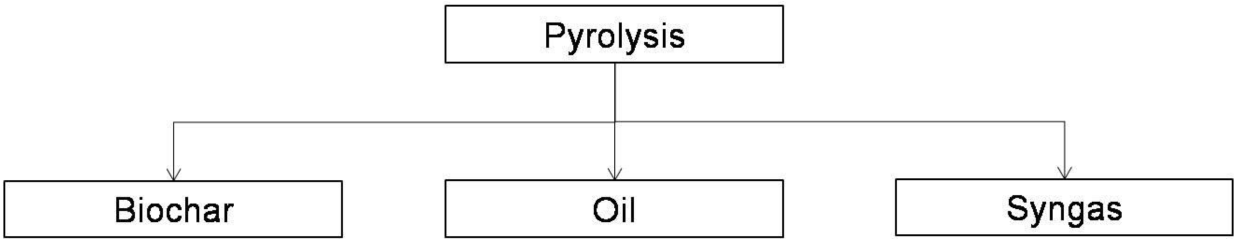


Figure 1 - Pyrolysis products

During pyrolysis, the biomass decomposes due to the high temperature, in absence of oxygen. It can be operated in different ways, modifying the process parameters, the most important being the temperature and the residence time.

Different type of pyrolysis are slow pyrolysis, intermediate pyrolysis and fast pyrolysis. As the name suggests, the main difference is the duration of the process, which goes from a few seconds to days.

Table 2- Overview of different pyrolysis type parameters.

| | T °C | Residence time | Products | Yields range [wt%] |
|---|---|---|---|---|
| **Slow** | 350-700 | Minutes to days | Biochar<br>Oil<br>Syngas | 25 - 35<br>20 - 50<br>20 - 50 |
| **Intermediate** | 400-500 | minutes | Biochar<br>Oil<br>Syngas | 25 - 40<br>35 - 50<br>20 - 30 |
| **Fast** | 300-1000 | seconds | Biochar<br>Oil<br>Syngas | 10 - 25<br>60 - 75<br>10 - 30 |

2) **Hydrothermal carbonization**. HTC is a thermal conversion process that converts the initial feedstock in a condensed carbonaceous solid product, called biochar, but sometimes also referred to as hydrochar. The feedstock is treated in an aqueous environment with temperatures between 150°C and 350°, for 30 minutes to 16 hours, under the pressure generated by water evaporation, with biochar yields between 40% and 70% (Rillig et al., 2010; Shackley et al., 2016). This technology requires that the feedstock has a high initial water content. This lead to the production of a biochar with high O content, that compromises its stability in the soil, making it more easily degradable (Hornung, 2014; Rillig et al., 2010; Schmidt et al., 2014).

   Among the parameters, temperature has been shown to be the most important. Carbonization temperature depends on the initial feedstock and its decomposition temperature. The produced biochar contains highly oxygenated functional groups (Jain, Balasubramanian, & Srinivasan, 2016).

3) **Gasification**. Gasification is a thermal conversion process whose main product is a gas phase composed of hydrogen ($H_2$), carbon monoxide (CO), carbon dioxide ($CO_2$),

methane ($CH_4$) and other trace gasses. The process involves the partial oxidation of the feedstock with steam, $CO_2$, $O_2$ or air at high temperature in under-stoichiometric oxygen concentration. The produced gas can be used as fuel for energy production or for power generation. Since the conversion level of carbon is about 95% the amounts of co-products and their carbon content are very low. However, gasification with fluidised bed produces fly-ashes with a carbon content up to 70%. Gasification operates with temperature higher than 700-800°C (Shackley et al., 2016).

Table 3 - Overview of gasification parameters

| | T °C | Residence time | Products | Yields range [%] |
|---|---|---|---|---|
| **Gasification** | 700-800 | Minutes to hours | Biochar<br>Oil<br>Syngas | 5 - 10<br>1 - 5<br>85 - 95 |

Average products yield for pyrolysis, HTC and gasification are reported in Figure 2. Hydrothermal carbonization yields are not included due to the great variability in the temperatures that can be applied, giving very different products yields.

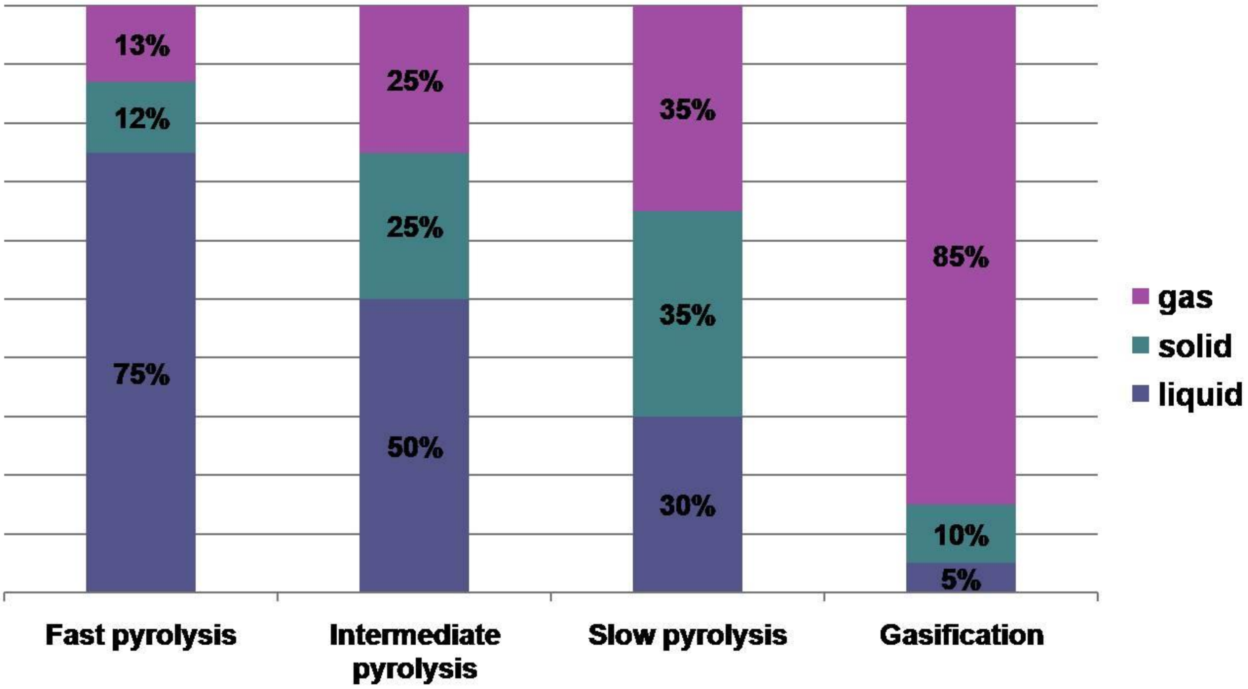


Figure 2 - Average yields of biochar, oil and gas from different production technologies and feedstocks.

### 1.3.4 Biochar activation and modification

To improve the properties of the biochar, treatments are often applied to activate it. To do this, acids, bases and oxidants can be used. These treatments have different effects on biochar. Some increase the surface sorption sites, others add functional groups on its surface that make it more reactive.

It has been proved that $H_2O_2$ oxidization can increased functional groups on biochar surfaces increasing biochar ability sorption capacity for lead (Yanmei et al., 2013). Another oxidant used for the treatment of biochar is $KMnO_4$.

Acid treatment requires biochar to be submerged or suspended in acid solutions with a ratio up to 1:10 (BC: acids) at a temperature from room to 120°C. HCl, $HNO_3$, $H_2SO_4$, and $H_3PO_4$ can be used (Zhang, Wang, & Sun, 2011).

Basic treatment generally involves the use of KOH and NaOH. These oxygenated functional groups provide sites upon which metal cations can be chemically sorbed. Acid-activated biochar was found to have a much higher capacity to absorb heavy metals than non-activated biochar (Petrović et al., 2016).

In general, the physical treatments for biochar activation are simple and cheap, but they are less effective than chemical treatments. The physical modification process requires the use of chemicals (Rajapaksha et al., 2016).

### 1.3.5 Thermo-catalytic reforming

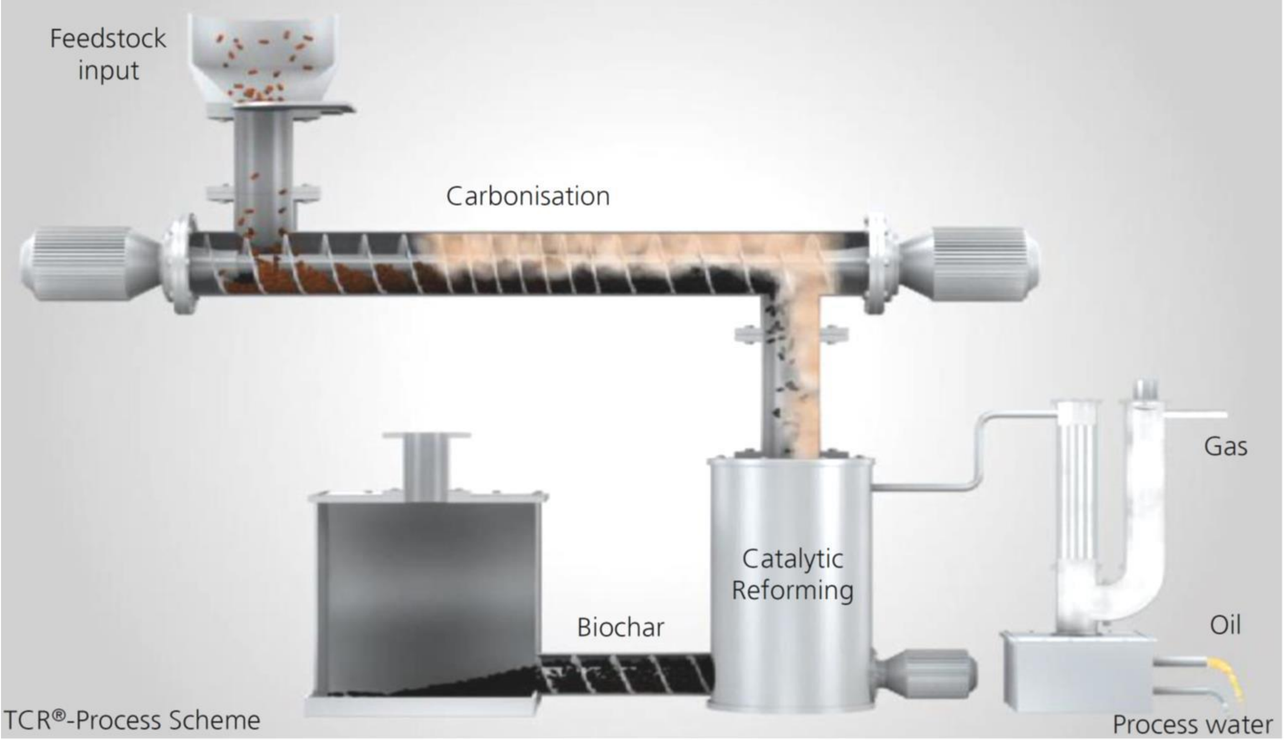


Figure 3 - TCR process scheme

The Thermo-catalytic reforming (TCR) technology was developed at the Fraunhofer Institute UMSICHT, Sulzbach-Rosenberg branch. A process scheme is shown in Figure 3.

The TCR combine an intermediate pyrolysis with an integrated downstream catalytic reforming step. The feedstock is converted into three the main products: biochar, syngas, and a liquid phase composed by both bio-oil and water. The liquid phase, also called condensate, can be subsequently separated by gravity.

Results have shown that the technology can produce a bio-oil with superior physical and chemical properties when compared with traditional fast pyrolysis oil, and a hydrogen-rich syngas. The TCR bio-oil is low in oxygen content, low in acidity and viscosity, phase separates from water, has a high calorific value and is completely miscible with conventional fossil fuels (Stenzel, Heberlein, Klinner, & Hornung, 2016).

Several feedstocks have already been tested with the process, and their products characterized. Tested feedstocks are, among others, digestate, municipal solid waste, woody biomass and sewage sludge. The feedstock moisture content cannot exceed 30wt%, otherwise the energy required by the system would increase, due to the heating of wet biomass. Feedstock with a moisture content up to 30% can be used without a previous drying phase (Conti et al., 2017a; Jäger et al., 2016; Neumann et al., 2015; Ouadi et al., 2017).

During the first stage the pyrolysis takes place. The feedstock is fed in the screw reactor through a hopper at a temperature of 400-450°C. Since the reaction requires an environment without oxygen, the reactor is flushed with nitrogen before the heating process.  There is a separation between volatile and non-volatile compounds, the first one being a vapuor phase, while the second one is the biochar. Then, all the products are conveyed into the post reformer where the catalytic reforming phase takes place, increasing the quality of the intermediate products. The solids and the vapours are processed in the post reformer in the presence of biochar, with a temperature up to 700°C, and they are then cooled down to ambient temperature. The vapours separate in a liquid (bio-oil) and in a gaseous phase (syngas).

The syngas is engine-ready, being composed of $H_2$, CO, $CH_4$, $CO_2$ and a small fraction of other compounds ($C_xH_y$).

The bio-oil is miscible with fossil- and bio-fuels. It has a high carbon and a low water content, low total acid number and high heating value. Its properties can be further increased by distillation and hydro-deoxygenation (Neumann et al., 2016).

The biochar has a high carbon and low hydrogen and oxygen content, which gives it a high stability when in the soil. Moreover, due to its high heating value, it can be used for heat and power production. The surface structure and area can be influenced during the reforming step. Depending from temperature and residence time they both can be increased (Stenzel et al., 2016).

The TCR process is also well suited to poor quality waste organic feedstocks (sewage sludge, paper industry residues, the organic fraction of municipal solid waste, anaerobic digestate and others) which are high in moisture and ash content (Conti et al., 2017b).

### 1.3.6 Environmental management and current applications of biochar

Biochar production can be a waste-to-resource process. Different kind of waste, such as municipal waste, animal manure, sewage sludge and agricultural residues can be used as feedstock for the pyrolysis process. Furthermore, organic waste is widely available and is currently not completely valorised in other ways (Hussain et al., 2017).

However, the benefits of biochar productions are maximized only when waste management and efficient application of co-products (i.e. syngas, oil) take place simultaneously (Hussain et al., 2017).

Different studies pointed out that the application of biochar on soil can change its properties. However, is not possible to assume that biochar application always reflects in an improvement of soil properties. As a matter of fact, the feedstock plays a fundamental role in determining if the application of biochar will lead in an increase in the crop yield or, on the contrary, to a stressful situation for the crop, resulting in lower yield and quality (Paneque, De la Rosa, Franco-Navarro, Colmenero-Flores, & Knicker, 2016).

The potential of biochar as soil amendment have been proved, but yet some uncertainties remain. A biochar with high SSA could help with water retention, but it may also prevent crops from getting enough water. For this reason, further experimentation should be done. Indeed, it has been observed that the biochar SSA is an important factor to consider. A high SSA, although increasing the water retention capacity of the soil can cause damage in case of drought periods. In contrast, a biochar with lower SSA makes the water more readily available. it is therefore important to take into account the water conditions of the soil on which biochar is to be applied, differentiating greenhouses from open fields (Paneque et al., 2016).

Analysis carried out in tropical soils in Zambia and Indonesia demonstrated that biochar application has several effects on nutrient availability and contaminant removal. In fact, $K^+$ and $Mg^{2+}$ concentration increase after the addition of biochar, while $Mn^{2+}$ concentration decreases in almost all the soils tested. $Al^{3+}$ concentration decreases exponentially due to the addition of biochar in all soils tested, with a rising of pH (Alling et al., 2014).

Biochar that was previously used as a filter can be enriched in some nutrients, such as N and P, and can be used in agriculture as soil improver. An important feature of biochar is the fact that it immobilize the nutrients and release them with a slow rate (P. Kim, Hensley, & Labbé, 2014). Some studies tested the ability of biochar to release nutrients that were previously manually added. Even if biochar is proven to be a good slow-release fertilizer, manually adding the nutrients will not help to deal with the end of their natural reserves (Kim et al., 2014).

Biochar application in soils brings another benefit, other than soil improvement. Thanks to its stable form, biochar acts as carbon storage. However, not all the technologies described above produce biochar that is stable in time. Its stability depends on the concentrations of oxygen and hydrogen, which must be very low. The carbon (C) content of biochar depends on the feedstock. Biochar from woody biomass has a greater C content than biochar from herbaceous biomass, with a range between 61% and 80%. Thanks to its high C content and stability, it has been stated that every ton of biochar applied on soil results in 0.60-0.81 ton of C that can be sequestrated, equivalent to 2.20-2.93 ton of $CO_2$ (Galinato, Yoder, & Granatstein, 2011; Oliveira et al., 2017).

Moreover, it has been proved that the addition of biochar to the soil reduce Nitrous Oxide ($N_2O$) emissions (Song et al., 2019). $N_2O$ is one of the most important greenhouse gases (GHG) because of its high Global Warming Potential (GWP) of 298 (the GWP of $CO_2$ is 1). $N_2O$ concentration has increased in the latest years and its residence time in atmosphere is about 100 years. Agricultural soils represent one of the sources of $N_2O$, due to the use of a large amount of nitrogen fertilizer.

### 1.3.7 Contaminants removal

A newer approach is to use biochar as a filter material. Biochar characteristics, such as SSA, and the presence of various functional groups on the surface, allows it to attract and adsorb pollutants both in soil and aqueous solutions.

These characteristics depend on the production process, as well as on the starting feedstock (Carey, McNamara, & Zitomer, 2015). Different process conditions and feedstock properties lead to differences in the structure and chemical composition of the biochar surface. It has been seen that high temperature biochar has a higher surface area (Sizmur, Fresno, Akgül, Frost, & Moreno-Jiménez, 2017) and a lower O/C ratio. This reflects in less hydrophilia and more aromaticity, due to the loss of polar functional groups that occur at high temperature (Chen et al., 2008). With the increasing of the temperature, both the BET surface and pore volume are likely to increase, due to the loss of volatile substance during the pyrolysis (Tan et al., 2015).

Biochar attitude to chemicals sorption have recently been investigated, especially with the purpose of nutrient recovery, due to concerns about the depletion of natural reserves (Novais, Zenero, Barreto, Montes, & Cerri, 2018).

Different studies showed that it is possible, in fact, to recovery P from water and subsequently extract it (Novais et al., 2018). Manyuchi et al., (2018) tested biochar filters for wastewater treatment, with recovery of 78% (w.t.) of the phosphate. In addition, biochar filters have shown good effects on other physicochemical characteristics of wastewater, such as Chemical Oxygen Demand (COD), Total Suspended Solids (TSS) and pH (Manyuchi et al., 2018).

However, even if the biochar attitude to sorb chemicals from water is evident, more studies needs to be done to investigate which feedstock are the better for biochar production and which modifications are the more suitable for specific chemicals removal.

## 1.4 Winery wastewater

Wine production is one of the leading sectors for food processing industry. In 2002, the world wine production was 261 x $10^5$ $m^3$. The main producer was Europe (69%), followed by America (9%), Asia (5%), Africa (4%) and Oceania (4%). The remaining 9% comes from small productions scattered around the world. In general, half of the production is generated by Italy, France and Spain (Bolzonella, Papa, Ros, Muthukumar, & Rosso, 2019; Brito et al., 2007). This kind of business affects the environment in differ ways: use of land, intensive use of water, use of pesticides, production of both solid and liquid wastes. In particular, water usage raise concern, due to the large amount used for the various washing activities (Bolzonella et al., 2019).

Details on Italian production for the year 2018 are shown in Table 4.

Table 4 - Regional wine production in Italy, divided by type (based on ISTAT data)

| | Type [L] | | | | | | |
|---|---|---|---|---|---|---|---|
| **Region** | **DOC w** | **DOC r** | **IGT w** | **IGT r** | **Table w** | **Table r** | **Total** |
| Abruzzo | 167 | 785 | 226 | 90 | 900 | 944 | **3112** |
| Basilicata | 0 | 27 | 11 | 15 | 4 | 29 | **86** |
| Calabria | 12 | 33 | 27 | 65 | 45 | 155 | **337** |
| Campania | 162 | 92 | 73 | 45 | 405 | 598 | **1375** |
| Emilia Romagna | 472 | 1127 | 1627 | 1318 | 2021 | 774 | **7339** |
| Friuli Venezia Giulia | 509 | 109 | 480 | 143 | 333 | 135 | **1709** |
| Lazio | 574 | 134 | 24 | 118 | 173 | 75 | **1098** |
| Liguria | 31 | 12 | 5 | 3 | 17 | 10 | **78** |
| Lombardia | 465 | 427 | 355 | 303 | 53 | 116 | **1719** |
| Marche | 21 | 110 | 53 | 103 | 197 | 204 | **688** |
| Molise | 6 | 26 | 29 | 26 | 103 | 275 | **465** |
| Piemonte | 1012 | 1466 | 0 | 0 | 58 | 122 | **2658** |
| Puglia | 219 | 464 | 924 | 1273 | 3458 | 3467 | **9805** |
| Sardegna | 378 | 204 | 35 | 87 | 37 | 100 | **841** |
| Sicilia | 752 | 843 | 1549 | 1003 | 493 | 349 | **4989** |
| Toscana | 163 | 1555 | 116 | 481 | 58 | 224 | **2597** |
| Trentino Alto Adige | 862 | 310 | 105 | 60 | 10 | 8 | **1355** |
| Umbria | 161 | 143 | 109 | 164 | 31 | 22 | **630** |
| Valle d'Aosta | 6 | 9 | 0 | 0 | 1 | 4 | **20** |
| Veneto | 7588 | 1243 | 1062 | 1162 | 1502 | 309 | **12866** |
| **Total** | **13560** | **9119** | **6810** | **6459** | **9899** | **7920** | **53767** |

A generic scheme of the phases in the wine production process is shown in  Figure 4.

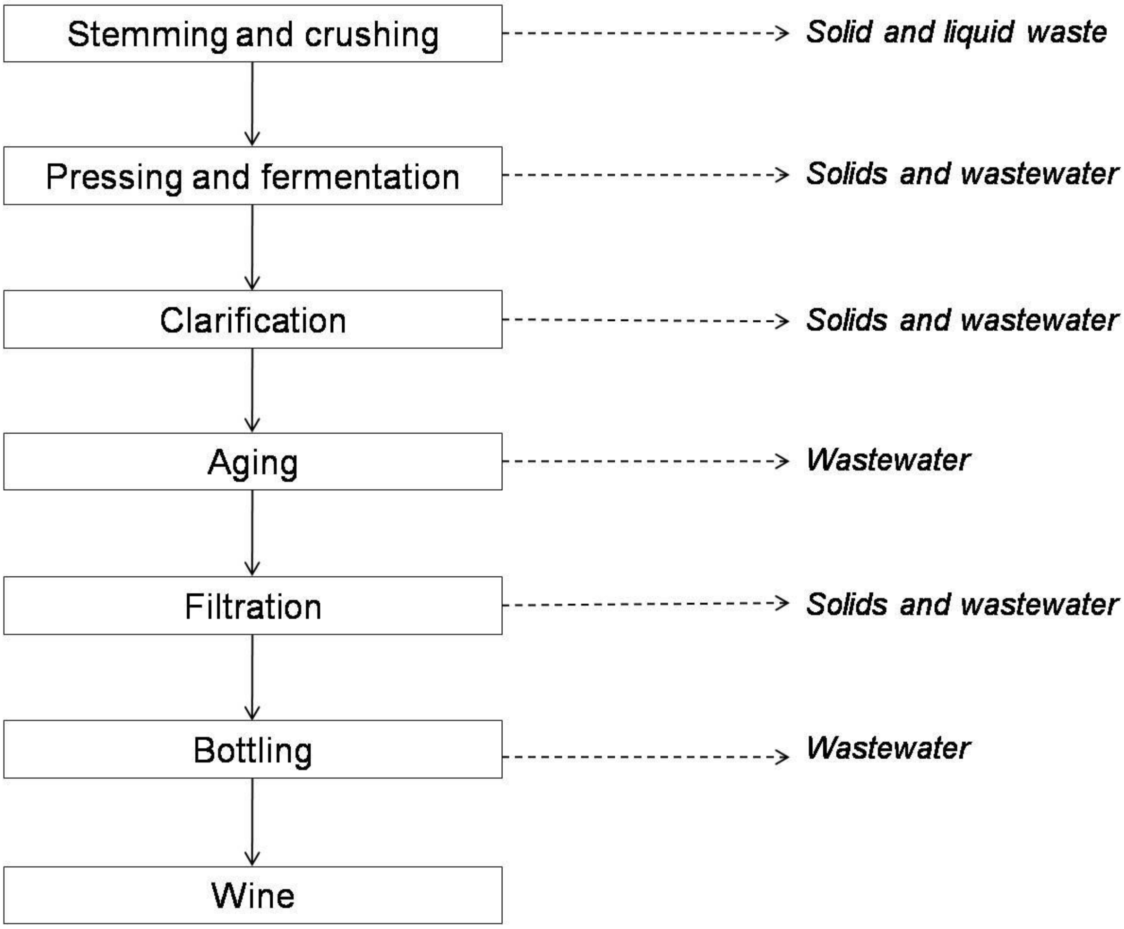


Figure 4 - Generic scheme of the wine-making processes and waste production.

During the first stage, the separation of grape stalks (stemming) takes part. After crushing, the juice is fermented. Then, juice and suspended solids are separated and, before packing, the juice is clarified and stabilized. All these processes produce a large amount of waste, both solid and liquid. In particular, wastewater are produced in all the steps (Bolzonella et al., 2019).

Wastewater can contain grapes, juice, alcohol, sugar, cleaning agents and other chemicals. Wastewater characteristics are different among wineries and depend on the wine type produced and on climate. In particular, the grape harvest, filtration, processing and bottling phases involve a massive use of water, which must be purified, when in contact with the substances released by the grape. Generally, wastewaters in wineries are characterized by high organic loading and salinity and low pH (Bolzonella et al., 2019). Water is also used to regenerate earth drum filters and ion exchange columns. In addition, it is used in cooling systems.

The amount of wastewater produced along the year varies greatly, being winemaking a seasonal activity (Brito et al., 2007). The principal pollutants can be divided in four categories:

1. Sub-product residues – stems, seeds, skins, lees, sludge, tartar, etc.
2. Loss of brut products – musts and wines due to accidental losses and during washings;
3. Products used for wine treatment – fining agents, filtration earths, etc.;
4. Cleaning and disinfection products used to wash materials and soils.

The important parameters that have to be monitored in wine production wastewaters are (Day et al., 2011):

- Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)
- Total Suspended Solids (TSS) and Total Dissolved Solids (TDS)
- Electrical conductivity
- Nutrients concentration
- pH
- Dissolved oxygen
- Salts, such as Na, K, Ca, Mg

Water used for cleaning is the biggest part of the water treatments in a winery. The amount of wastewater in wineries is almost equal to incoming water, due to the fact the water is not used in the final product (Garcia, Loewen, Oland, Garn, & Britain, 2018).

Due to the complex composition of winery wastewater, its treatment can be difficult. The main objective is to reduce the amount of organic compounds, as well as to reduce the concentrations of nitrogen and other fertilizers (Garcia et al., 2018). It is possible however, when some parameters are respected, such as pH, salinity and heavy metals concentration, to spread wineries wastewater on agricultural land (Ercoli, Bonari, & Produttiva, 2017).

Treatment systems include physical, biological and chemical processes. Physical processes main consists in sieving and filtering. Biological treatments include anaerobic and aerobic treatment of the effluent. Chemical treatments often consist in pH adjustment (Garcia et al., 2018).

Both anaerobic and aerobic treatments are suitable for the degradation of organic matter, with the anaerobic one being more economical and the aerobic one more effective. Often, both technologies are applied. Since the majority of the organic matter in the wastewater is in soluble form, a static sedimentation unit is not effective (Bolzonella et al., 2019; Brito et al., 2007).

Different type of wastewater treatment systems are lagoons, bioreactors, membrane bioreactors, sequencing batch reactors, activated sludge, constructed wetland and wetland biofilters (Garcia et al., 2018).[3]

Lagoons are open ponds specifically designed to treat organic matter. They require low energy inputs and are cost effective for big wineries. However, they require large areas where to be installed and periodic dredges.

Bioreactors are containers with microorganisms able to degrade organic matter. They are effective in diminish organic matter and nitrogen content and have a very low footprint. Some of them require significant amount of energy.

Artificial wetlands use plants, instead of microorganisms, to remove organic matter from the water. Wetlands are easy to manage and do not require large amount of energy. However, they need large areas and need to be maintained through the removal of accumulated material.

Activated sludge is a system that comprehend the mix of wastewater and microorganism to reduce organic matter.

In recent years physical treatments, like filtering, have been resumed. The effectiveness of activated carbon and biochar in the removal of organic matter and nutrients has also been tested for winery wastewaters (Carey et al., 2015; Huggins, Haeger, Biffinger, & Ren, 2016).

Biochar and activated carbon performance in wastewater treatment have been compared and, even if activated carbon is a well know and more common filter material, biochar shows better performance when it comes to complex wastewaters. That can be explained by the difference that exists between the pores of the two materials. Biochar pores are often bigger (macropores)

---

[3] http://waterandwine.bloomcentre.com

the activated carbon pore smaller (micropores). Activated carbon micropores get blocked more easily and, thus, are less effective (Huggins et al., 2016). However, as mentioned above, the characteristics of biochar depend on many parameters, and therefore it is not possible to assume that the performances will always be the same.

## 1.5 Biochar as a filter material

### 1.5.1 Removal of inorganic pollutants

Due to their non-biodegradability and bioavailability, metals are highly toxic to living organisms, as they can be bioaccumulated and can therefore interact with the body's functions. Heavy metals removal has been studied for years now, being an important phase in wastewater treatment. Even if lots of different removal method do exists, the problem become even more challenging when it comes to low concentrations (Pellera et al., 2012).

The ability of the biochar to retain inorganic pollutants from aqueous matrices has been proved for different elements.

Biochar from different feedstock, such as rice husks, olive pomace, orange waste and crop straw, has been tested for Cu (II) removal from aqueous solution. The performance is dependent on different parameters, the most important are pH, Cu (II) initial concentration and contact time (Pellera et al., 2012; Tong, Li, Yuan, & Xu, 2011). In addition to aqueous solutions, the ability of biochar to remove Cu (II) was also tested with synthetic water and soil solutions. Although biochar is effective for this scope, biochar that has been previously activated is able to absorb more Cu (II) (Trakal, Šigut, Šillerová, Faturíková, & Komárek, 2014).

Cadmium removal was tested using both activated and non-activated hydrochar. Activated hydrochar showed a $Cd^{2+}$ removal capacity close to 100%, better than non-activated hydrochar. Also in this case the sorbent performance was dependent on the pH of the solution, on the biochar quantity, and on contact time (Regmi et al., 2012).

Lead sorption was also investigated, using biochar from anaerobically digested biomass. In this case the performance was really high, almost comparable to activated carbon performance (Inyang et al., 2012).

Biochar has therefore proved to be an excellent tool for removing heavy metals from aqueous solutions. However, it is more efficient in the removal of Cu (II) compared with the removal of other metals, like $Cd^{2+}$, when these are simultaneously present in aqueous solutions (Inyang et al., 2012).

### 1.5.2 Removal of organic contaminants from water

Sorption of organic contaminants from water onto biochar occurs due to its high surface area and microporosity. Biochars produced at a temperature larger than 400 °C in particular are more effective for organic contaminant sorption.

Surface polarity and aromaticity are important characteristics of biochars, as they affect aqueous organic contaminant sorption. In general, at a temperature larger than 500 °C, biochar surfaces become less polar and more aromatic due to the loss of O- and H-containing functional groups, which may further affect organic contaminant adsorption.

Therefore, the functionality of the target organic contaminant is critical to the biochar adsorption capacity. Electrostatic attraction/repulsion between organic contaminants and biochar is another possible adsorption mechanism. Biochar surfaces are normally negatively charged, which could facilitate the electrostatic attraction of positively charged cationic organic compounds. Solution chemistry, such as pH and ionic strength, may also affect the sorption of organics onto biochar. (Ahmad et al., 2014)

### 1.5.3 Nutrient accumulation

Due to its sorbing capacity, biochar can be used to recover nutrients from wastewater streams.

Previous studies show that biochar can sorb N and K from wastewater streams, with or without previous activation (Carey et al., 2015). Organic matter content reduction has been investigated as well, since food manufactures around the world produce wastewater streams with high organic content (Barber, Yin, Draper, & Trabold, 2018a).

However, as said before, feedstock, pyrolysis condition and activation techniques affect the adsorptive capacity of the biochar (Carey et al., 2015). Especially for organic matter removal, the initial feedstock has a crucial role on biochar performance (Barber et al., 2018a).

### 1.5.4 Activated carbon

Activated carbon is a C rich, porous material, typically used for fluids filtration. The first records date back to ancient Egypt, when it was already known for its adsorbent characteristics and, in recent years, as a filter in gas masks. The adsorptive capacity derives from its high surface area, in general greater than 1000 $m^2/g$ (Rodríguez-Reinoso & Marsh, 1992), produced by either a combination of heat and pressure, or with strong acid or base followed by carbonization, to make it highly porous.[4]

AC is usually produced in three forms: pellet, granular and powder, the last two being the most popular. Powder and granular AC represent respectively the 60% and 30% of the global market, which in 2018 was estimated at 4,72 billion United States Dollars (USD). The market is expected to growth due to the increasing need for water and sewage treatment[5]. AC can be produced from any carbonaceous feedstock, fossil, waste and renewable. However, different feedstocks mean different adsorbent capacity. It was noticed that AC made from animal's bones had a higher adsorbent capacity than AC made from wood.

It was also noticed that, regardless of the feedstock used, some pore in the AC where already "occupied" right after the production. This could be due to the ash content, which often fits into the pores, obstructing them. To overcome this problem, activation is required. The first type of activation is the thermal activation, which remove compounds from the surface of the skeleton, thus increasing the availability of pores for absorption (Hagemann et al., 2018).

Activated carbon production processes commonly include feedstock pre-treatments like grinding, blending, and agglomerating, followed by carbonization and activation. A flow diagram illustrating the production process of activated carbon can be seen in Figure 5.

---

[4] https://www.grandviewresearch.com/industry-analysis/activated-carbon-market

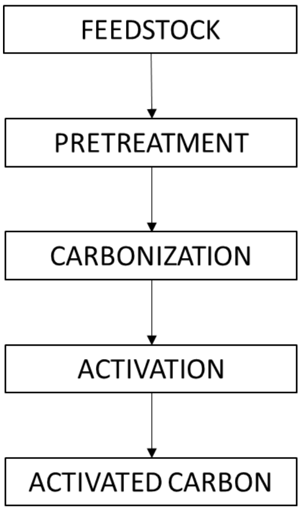


Figure 5 - AC production process flow diagram

### 1.5.5 Zeolite

Zeolites are hydrated aluminosilicates made of alkaline and alkaline-earth metals. Zeolite has uniformly sized pores throughout its crystal structure. In nature there are 40 types of zeolites and 150 have been synthesized. The most common natural zeolites are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. The most common synthetized are zeolites A, X, Y, and ZMS-5.

The markets are different for natural and synthetized: the first ones are mainly used as pet litter, animal feed, horticultural applications (soil conditioners and growth media), and wastewater treatment, while the other as catalysts, detergents and molecular sieves. [6]

Zeolites market was evaluated at 29.08 billion USD in 2016 and expected to grow at a composed annual growth rate of 2.5% by 2022.[7] Their average cost is about 88 USD/kg (Blaszczak, 1999).

---

[6] https://www.usgs.gov/centers/nmic/zeolites-statistics-and-information

[7] https://www.grandviewresearch.com/industry-analysis/zeolites-market

## 1.6 Italian fertilizer regulation

The Italian regulation about fertilizers refers to the D.Lgs. 75/2010 and subsequent changes. Here a large number of materials are listed and described. Only the materials in this list can be used in field to improve the soil quality. The benefits derived from these fertilizers can be general or more specific, e.g. incrementing the available N amount for crops.

It is possible to ask for the addition of new matrices or products to the list, after the technical commission favorable opinion (art. 10 D.Lgs 75/2010). For this reason, in 2012, the Italian Biochar Association (ICHAR) presented a motion to the Government asking to add biochar to the list of soil conditioners (‘‘ammendanti’’). Afterwards (2015) the Ministry Of Agricultural, Food And Forest Policies agreed on including biochar as soil conditioner and formalized it by publishing on the ‘‘Gazzetta Ufficiale della Repubblica Italiana’’, n.186, 12-08-2015 some changes to Annexes 2 and 7 of the D.Lgs. 75/2010. Biochars from pyrolysis and gasification were added to the list of soil conditioners, with a short description of the products and some quality criteria. Quality categories are made based on these criteria, for example on the organic carbon content. In Annex 7 the tolerance values for some parameters have been added.

Table 5 - Biochar from pyrolysis and gasification characteristics

| $C_{org}$ tot | pH | Ash | Humidity | Salinity [mS/cm] |
|---|---|---|---|---|
| >20 | 4-12 | >0.7, <60 | >20 | <1000 |

Other elements or useful substances which must be quantitatively declared are grain size, total nitrogen, total potassium, total phosphorus, total calcium, total magnesium, total sodium, %C from carbonate, phytotoxicity test and growth, maximum water retention.

As said before only biochar deriving from pyrolysis and gasification is considered as a soil conditioner in the decree. Moreover, only certain feedstocks are officially recognized. They are products and residues of vegetable origin from agriculture and forestry, as well as from olive pomace, pomace, bran, hazelnut and fruit shells, untreated wood processing waste, as a by-product of related activities. Other feedstock such as animal manure or other animal derived biomasses are excluded. In addition, it is not specified if it would be possible to use, as a soil conditioner, biochar that has been previously used for other purpose, for example as a filter material for wastewater.

# 2 MATERIALS AND METHODS

## 2.1 TCR®2

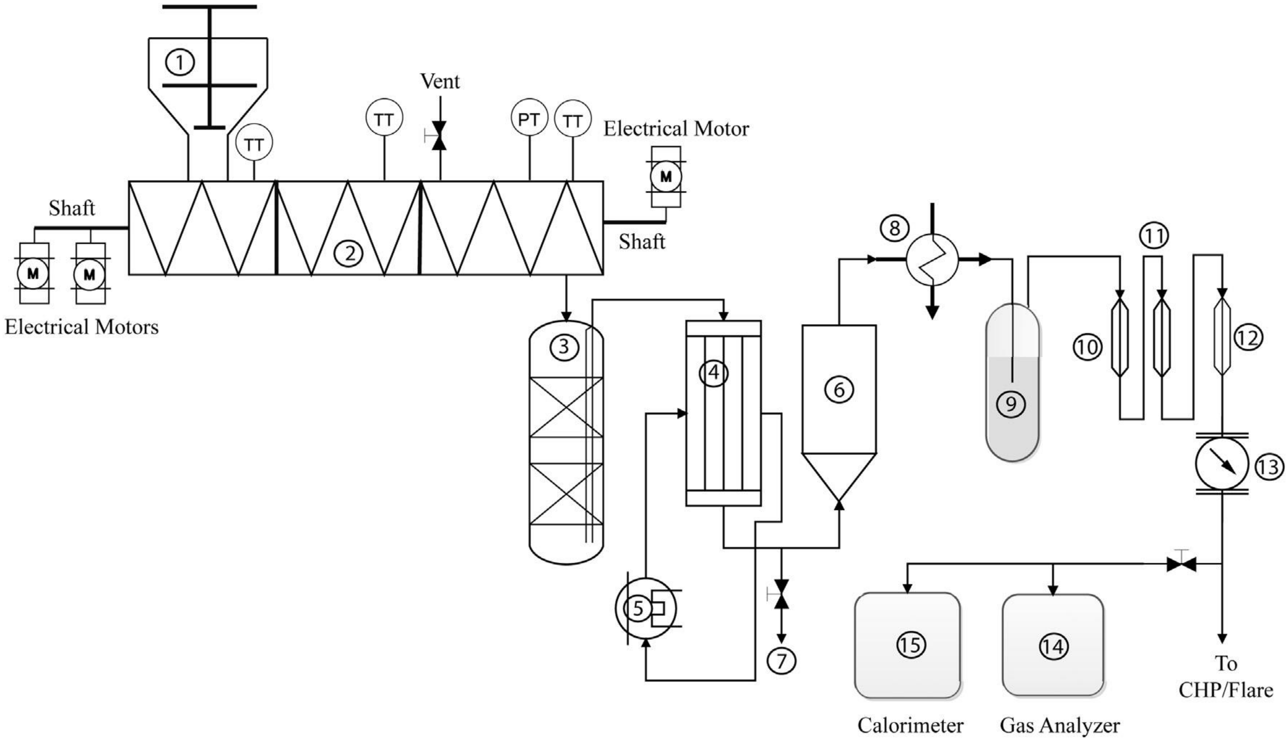


Figure 6 - TCR®2 laboratory plant diagram

The TCR®2 reactor is a lab scale TCR® reactor that operate with up to 2 kg per hour. Figure 6 shows the TCR2 scheme with the main components. The pyrolytic chamber (2) is fed by a hopper (1). The feedstock moves thanks to two screws. In this phase char and vapours are formed. Then, everything is poured into the post-reformer (3). Here the vapours react with some biochar previously added and the newly formed one. This is the part of the TCR® that gives the products their superior characteristics. Subsequently, the vapours are cooled (4) and collected through a glass bottle (9) and the gases are analysed by a gas-analyser (14) and the calorimeter (15), after passing through the filters (10-12).

Before every trial, the TCR®2 reactor was disassembled and cleaned. The reforming unit was then filled with 225 g of biochar from previous experiments, produced by a similar feedstock. Also, the gas washing bottle was filled with water from woody biomass TCR treatment. In the end, the whole apparatus was reassembled. Since pyrolysis requires the process to take place in the absence, or with very low concentrations, of O, the reactor is initially flushed with N. Once the O concentration was below 0.1%, the N flux was stopped. The reactor and the post-reformer need to be pre-heated. It is possible to set two different temperatures for the two parts. When the desired temperature was reached, the two screws inside the reactor were started at the same moment.

The biochar remains in the post-reformer, until the end of the trial, then it is collected after cooling the reactor. Thanks to its long residence inside, at high temperature, it is free from any condensation product.

During the trial, every 15 min the gas flow meter reading was recorded, while the gas-analyser and the calorimeters data were recorded automatically. The trial was stopped when no more gas flow was detected.

When the trial ended, the heaters were stopped, and the reactor was left to cool overnight.

## 2.2 Biochar production

### 2.2.1 Feedstock

The raw material used for biochar production was vine pruning, supplied by an Italian vineyard.

Before the pyrolysis process, the feedstock was grinded with an Erdwich brand shredder, in order to obtain a more suitable size, because its initial shape and size would not have allowed its use in TCR®2. The material obtained was extremely heterogeneous in size, with dimensions ranging from powder to 4/5 cm long pieces.

The feedstock was characterized by measuring its calorific value, through bomb-calorimeter, and by measuring water and ash content.

### 2.2.2 Biochar production

During the pyrolysis, the heterogeneity of the material was a problem. In fact, the feedstock repeatedly stuck in the feeder, producing sudden pressure changes inside the reactor. In the end, it was decided to resort to a quick pre-treatment of the feedstock by selecting, with the help of a 1 cm sieve, only the largest fraction of the material, in order to avoid further material jams.

As previously said, differences in temperature lead to differences in the biochar behaviour as filter material. Two different types of biochar were produced to compare performances, the main difference being the temperature of the post-reformer. The first biochar, named

BC700, was produced with the post reformer at 700°C. The second biochar, named BC500, was produce with a post-reformer temperature of 500°C.

### 2.2.3 Biochar characterization

The water content in the feedstock was determined by measuring the initial weight of a sample, and the weight of the sample after being placed in a stove at 105°C for 24 hours.

Later, the same sample was used for measuring the ash content. The sample was placed for 24 hours in a stove at a temperature ranging from 500°C to 550°C. The difference between the weight of the sample after the evaporation of the water and the weight after further heating represents the quantity of ash contained in the feedstock.

The exact procedure is described below:

- Three samples were prepared using containers of known weight, adding an arbitrary quantity of feedstock and calculating the weight of the feedstock by difference.
- The samples were then placed in the oven at 100°C for about 24 hours
- After this time, the samples were removed from the oven and cooled in a closed glass container. Then the weight was again measured.
- Subsequently, the samples were placed in another furnace, at 500-550°C for one day, to determine the ash content. Then, the samples were allowed to cool for an hour in the oven at 100°C and then in a glass bowl. The weight of the ashes was determined by difference between the final weight and the initial weight of the bowl with the original feedstock sample.

The BET method was used to calculate the surface area of porous materials such as activated carbon and biochar. BET measurement is based on gas adsorption. To determine the specific surface area, the amount of gas absorbed by the material under examination is measured.

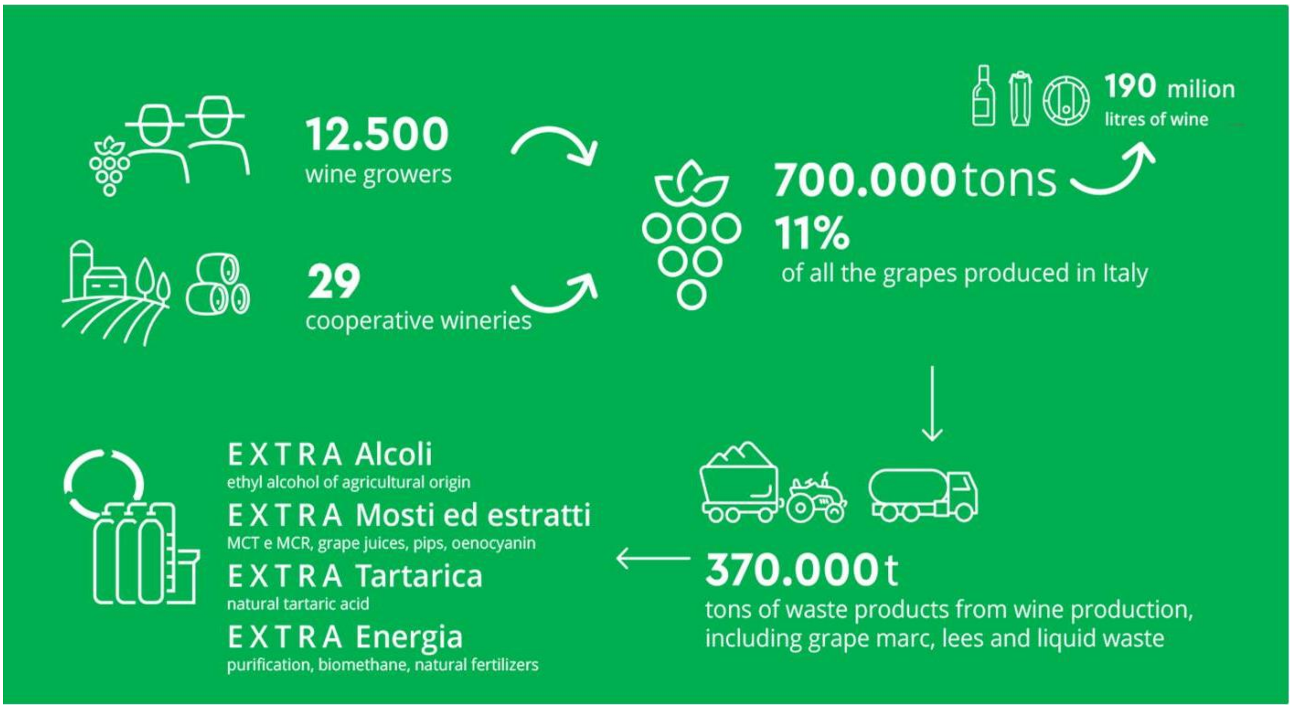
The samples were prepared for 1 hour at 350°C under vacuum. The measurements were then carried out according to DIN ISO 9277, on a Quantachrome NOVA4200, with carbon dioxide, at 0°C as a multipoint BET. ISO 9277:2010en and DIN ISO 9277:2013 standardize the methodology for the determination of the surface area applying the BET theory.

Due to the small dimensions of the biochar pores, BET surface was determine using $CO_2$ instead of N or Ar. The motivation lies in some limitations due to the use of nitrogen. At the low temperatures required for the operation, the nitrogen becomes poorly mobile, leading to an underestimation of the SSA. $CO_2$ avoids this problem, having proved to be the best solution at low temperatures (K. C. Kim, Yoon, & Bae, 2016).

The calorific value is an expression of the energy content per unit of mass or volume, quantified by the release of heat when burnt in air. The calorific value of both biochars was determined through a Mahler bomb-calorimeter. The heat generated from the combustion of a known amount of fuel is absorbed by water (or another liquid), whose temperature consequently increases and allows the calorific value to be measured.

Elemental analysis (CHNS) of the raw materials and products (bio-oil and biochar) was performed by using a Vario Macro cube elemental analyser from Elementar. The O content was calculated by difference (100-∑CHNS and ash content).

## 2.3 Case study: Caviro EXTRA



Caviro is one of the biggest cooperative of winery in Italy: 12,500 winegrowers from seven regions provide Caviro with 10% of the Italian grapes, equal to 700,000 ton/year.

The division Caviro Extra operates beyond the winery, it is indeed a perfect example of biorefinery. Along the supply chain a considerable quantity of by-products is produced, part of these as waste. Currently, the waste is mainly exploited for the production of energy, but also for the production of new products with high added value.

Caviro EXTRA consists of four divisions:

1. **EXTRA Alcoli:** Caviro EXTRA is an Italian market leader for the production of alcohol. At the Faenza plant, 90 million litres of alcohol, which is 100% bio-based, are produced per year. Thanks to its high quality, the alcohol can be used in various fields, such as food, pharmaceutical, cosmetic, energy, etc.
2. **EXTRA Mosti ed estratti:** the division develops a range of ingredients with high added value which can be employed in many industrial sectors. The main sectors are the food industry, oenology and vinegars, para pharmaceuticals, nutraceuticals and cosmetics. The division obtains the grape pips required by the food and para-

pharmaceutical industries and it also extracts oenocyanin, a natural red food colouring.

3. **EXTRA Tartarica:** the division produces natural tartaric acid – complying with the 100% bio-based carbon requirement – derived entirely from the sub-products of the wine-making industry, like wine marc and wine lees. The plants are based in Treviso and Faenza. The most interested sectors are the food industry, pharmaceuticals, chemicals and constructions sectors.
4. **EXTRA Energia:** Caviro EXTRA produces biogas and biomethane thanks to the anaerobic digestion plants in which the wastes from the processing of the by-products of the winemaking and of the wastewater supplied by Italian agri-food companies are treated. The new plant has a production capacity of 12,000,000 Nm3 of advanced biomethane.

The wastewater samples that the company provided for filtering experiments derive from this latest business unit.

### 2.3.1 Wastewater

Caviro supplied us with two wastewater samples 5 L each. These samples were characterized to determine the initial concentrations of compounds and elements and then compared with those obtained after the treatments.

The sample “Chiaro Flottatori” comes from the floatation process of the digested material produced by the anaerobic digestion plant. This plant treats distillery and other agro-industrial process wastes. Anaerobic digestion occurs under mesophilic conditions, at about 37 ° C. The outgoing sludge goes through a settling basin, whose average temperature is 30-35 ° C during the year. At this temperature the polyelectric-mediated floatation process takes place. Every year about 215,000 cubic meters of this type of wastewater are produced.

The sample “Chiaro Centrifughe” comes from the process of centrifuging the sludge from the thickening basin, into which the digestates of the anaerobic digestion plant, sludge from the oxidative process, and the sludge coming out of the floatation units are mixed together. These sludges are originated from distillery activities and from sludge coming from agro-industrial processing. The temperature of the centrifuged sludge varies between 25-30 ° C. Centrifugation takes place in the presence of polyelectrolyte as an adjuvant. The sample used for the analysis consists of the clarified part of the sludge. About 555,000 cubic meters of “Chiaro Centrifughe” wastewater are produced every year.

## 2.4 Wastewater characterization

### 2.4.1 Dry matter

For the determination of the dry matter in wastewater, a thin layer of water was placed into a glass container. Three repetitions (5.0 mL) of each sample were made. The dry matter was calculated both on the sample as is and on the filtered sample with a 0.45 µm syringe filter. For the unfiltered sample, the solids were resuspended by manual agitation.

The glasses were then put for 24 hours in the muffle furnace, at a temperature of 100°C, then allowed to cool. Finally, the new weight was measured.

The glass containers were weighed empty, after adding the 5.0 ml of sample and once they were taken out of the furnace and cooled. A Mettler Toledo ME204 weight scale was used to do the measurements.

### 2.4.2 Chemical Oxygen Demand

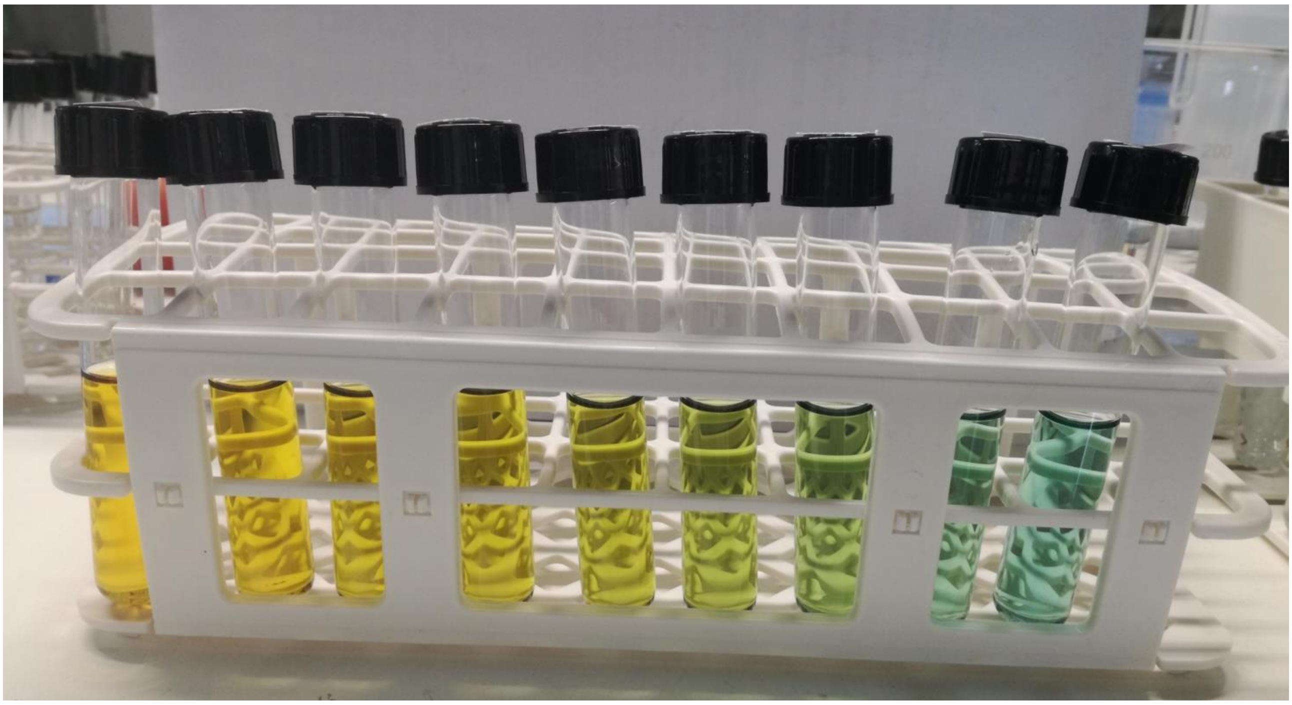


Figure 7 – Samples for the COD determination

COD is the measure of the amount of oxygen needed to oxidize organic compounds present in a water sample. COD tests are based on the assumption that the organic compounds present in the water can be oxidize in $CO_2$ through a strong oxidizing agent, in acid conditions. It takes about 3 hours to be completed.

The COD measurements (see Figure 7) were made according to the “Method 410.4, Revision 2.0: The determination of Chemical Oxygen Demand by semi-automated colorimetry” by the United States Environmental Protection Agency (EPA), using the spectrometer “UV-1900” from Herstellers Shimadzu Deutschland GmbH.

A sample of water was oxidized with a solution of potassium dichromate ($K_2Cr_2O_7$), with silver sulphate ($Ag_2SO_4$) as catalyst. In a 10 ml cuvette,1.5 ml of $K_2Cr_2O_7$ are added. Then 2.5 ml of sample were added and the solution mixed. The reaction starts just after the addition of 3.5 ml of $Ag_2SO_4$, the catalyst. Once closed tight and after mixing, the cuvette was heated at 150°C in the heating box (heated in advance) for two hours. The cuvette needed 30 minutes to cool down. After that, it was possible to proceed with the measurement.

A calibration curve, showed in Figure 8, was prepared using solutions with known COD concentration.

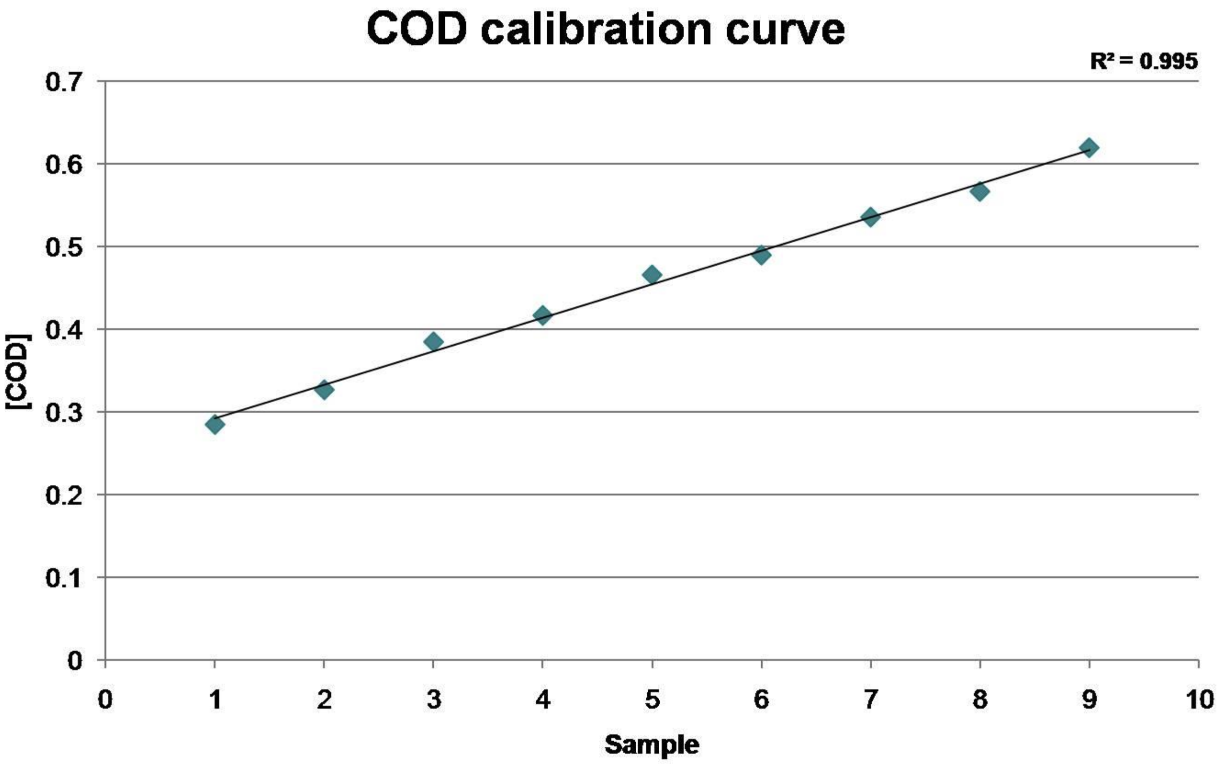


Figure 8 - COD calibration curve for concentration between 200 and 1000 mg/L

### 2.4.3 Nitrate-N cell test

For the determination of nitrate ($NO_3^-$) content a cell test provided by Merck KGaA Company, for concentrations between 0.5 and 25.0 mg/L $NO_3^-$ - N, was used (see Figure 9). Samples were diluted twenty times before measurement with deionised water.

The method used for this test is analogous to DIN 38405-9. The concentration was determined using the “Spectroquant® NOVA 30” from Merck KGaA.

In the reaction cells provided by the kit, 1.0 ml of the sample was added, followed by 1.00 ml reagent $NO_3$-1K. After mixing, the cell test became very hot and needed 10 min for the reaction to happen. After that, the sample was measured in the photometer.

In sulphuric and phosphoric solution. nitrate ions react with 2,6-dimethylphenol (DMP) to form 4-nitro-2,6-dimethylphenol that is determined photometrically.

Figure 9 – Nitrate cell test kit and cuvettes, from Merck KGaA Company

### 2.4.4 Chloride cell test

For the determination of the chloride ($Cl^-$) content a cell test provided by Merck KGaA Company, for concentrations between 5 and 125 mg/L was used (see Figure 10). The samples were diluted hundred times with deionised water before the measurement.

The method used for this test is analogous to EPA 325,1 and APHA 4500-$Cl^-$ E. The concentration was determined using the “Spectroquant® NOVA 30” from Merck KGaA.

In the reaction cells provided by the kit, 0.50 ml of the reagent $Cl^{-1}K$ was added, followed by 1.00 ml of the sample. After mixing, the sample was measured immediately in the photometer.

In the cell, $Cl^-$ reacts with mercury (II) thiocyanate to form slightly dissociate mercury (II) chloride. The thiocyanate released in the process reacts with iron (III) ions to form red iron (III) thiocyanate that is determined photometrically.

Figure 10 - Chloride cell test kit and cuvettes, from Merck KGaA Company

### 2.4.5 Ammonia nitrogen determination

The $NH_4^+$ - N measurements were made in two different ways, both adapted from DIN 38 406 - Teil°5 method. Firstly, a Merck KGaA Company kit was used, and then without the kit, but applying a methodology coherent with it.

For the ammonia nitrogen determination, the samples were diluted twenty times, since the range of determination of both tests was between 4 and 80 mg/L.

4.0 ml of reagent 2.6.3, 1.9 ml of deionised water, 0.1 ml of sample (diluted), and 4.0 ml of reagent 2.6.2, were added in a cuvette, in this order. After 1 hour it was possible to measure the sample with the spectrometer “UV-1900” from Herstellers Shimadzu Deutschland GmbH.

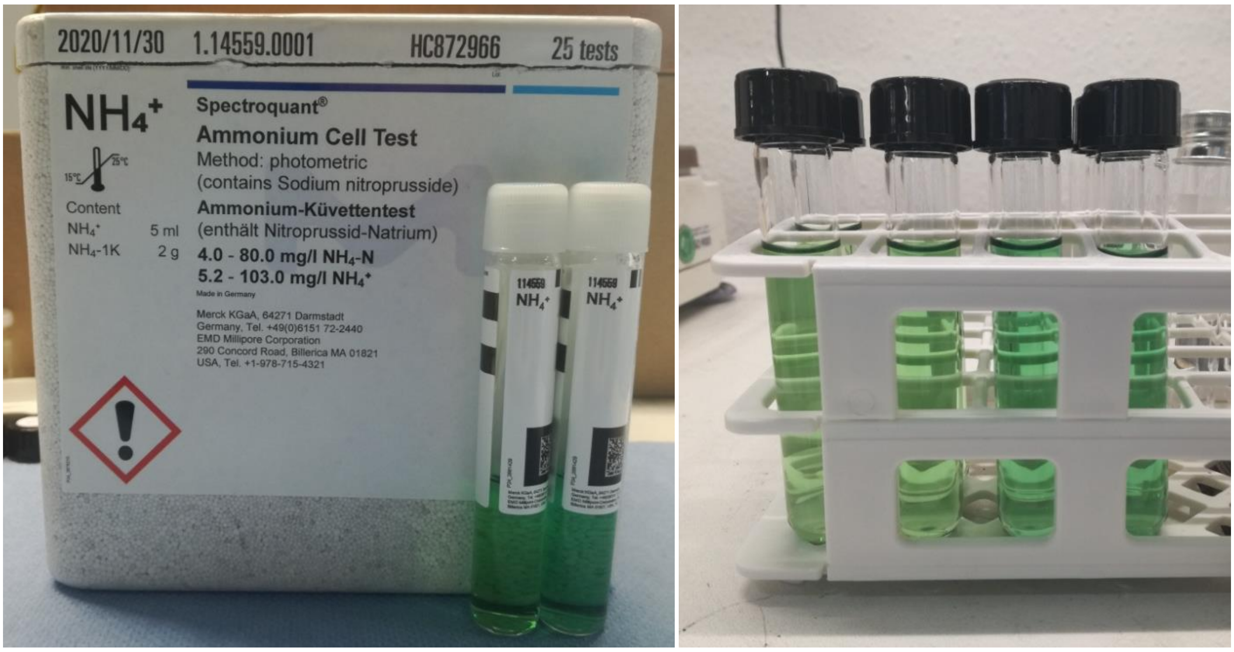


Figure 11 - Ammonium cell test kit and cuvettes, from Merck KGaA Company

### 2.4.6 Orthophosphate phosphorus determination

Orthophosphate ions were determinaed in two different ways, both adapted from DIN EN ISO 6878:2004 method. Both methods return the P content in orthophosphate ions as a result.

The firsts determinations were made with a Merck KGaA Company kit (see Figure 12). In the reaction cells provided by the kit, 0.20 ml of the sample was added, followed by 1 dose of reagent P-1K. After mixing, the sample was measured in the photometer “Spectroquant® NOVA 30” from Merck KGaA.

In sulphuric solution orthophosphate ions react with molybdate ions to form molybdophosphoric acid. Ascorbic acid reduces this to phosphomolybdenum blue (PMB) that is determined photometrically. The method is also analogous to EPA 365.2+3 and APHA 4500-P E.

The other measurements were made with a method adapted from ISO 6878:2004 method. The method involves the use of two different reagents: reagent 4.1.5, ascorbic acid ($C_6H_8O_6$), and reagent 4.1.6, a solution of molybdate acid. In a 10 ml cuvette 9.3 ml of deionised water, 0.1 ml of sample, 0.2 ml of reagent 4.1.5 and 0.4 ml of reagent 4.1.6, were added.

This method allows the determination of only orthophosphate ions, thus only ions which are already in the solution. With this method it is not possible to determine the total phosphate amount.

Figure 12 - Phosphate cell test kit and cuvettes, from Merck KGaA Company

## 2.5 Wastewater sorption tests

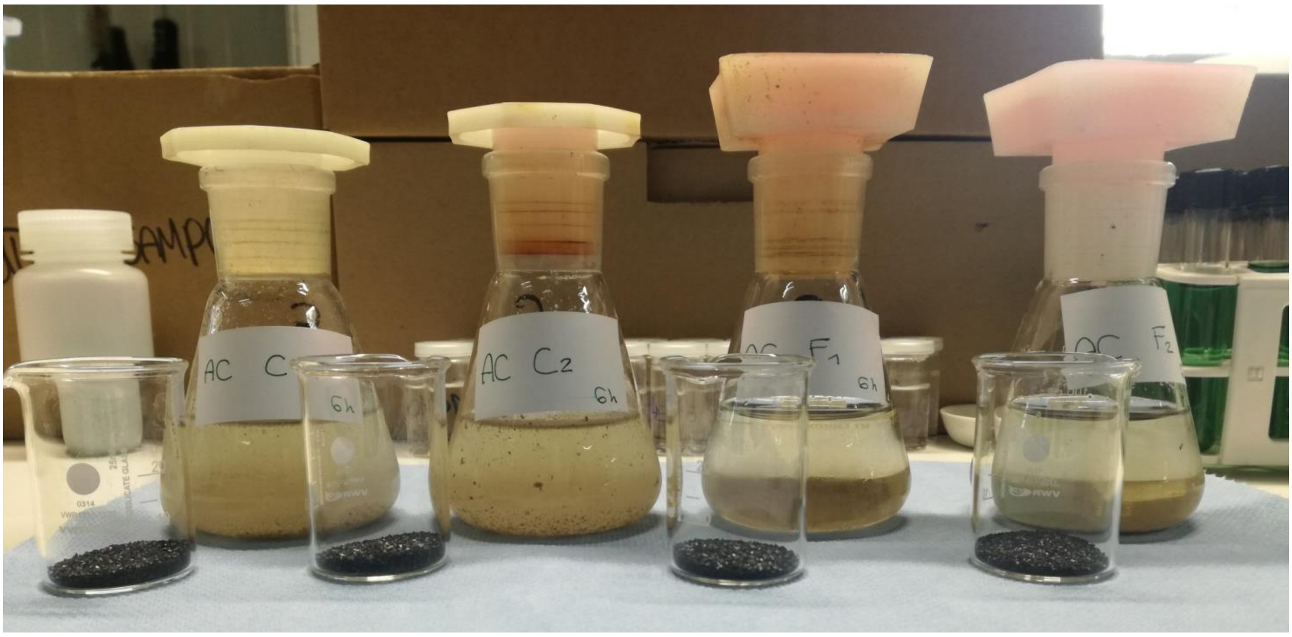


Figure 13 - Sorption test with wastewaters and activated carbon

To test the biochar's performance as a filter material, eight experiments were designed in which a known amount of biochar was placed in a flask containing wastewater. Both biochars were tested on both Caviro EXTRA wastewaters.

In order to better evaluate biochar performance, other types of commercial filter materials have been used for comparison: activated carbon and zeolites.

For the sorption test, a 1:50 ratio has been used. The characteristics that have been checked for each sample were: COD, $NH_4^-$ , $PO_4^{3-}$ and $Cl^-$. In order to understand how the sorbed quantity varied over time, four different experiments were performed with different contact times.

Each experiment was carried out under the same conditions, using 75 ml of wastewater at room temperature (about 23°C) and 1.5 g of the filter material, that were placed in 100 ml flasks closed with tops or parafilm. Then the flasks were placed in a shaker for the different time lengths. The continuous movement of the shaker allowed all the water to come into contact with the filter material. Furthermore, in this way the lightest part of the biochar did not remain on the surface.

Two repetitions were done for each wastewater-biochar combination.

Once the desired contact time was reached, the samples were filtered. The first step was to filter the samples with 5 -13 µm paper filters, to immediately interrupt the contact between the water and the filter material. Subsequently, the samples were further filtered with 0.45 µm syringe filters.

After that, the analyses were carried out. COD measurements were made immediately after filtering. Then, the concentrations of $NH_4^+$ - N, $PO_4^{3-}$ - P and $Cl^-$ were measured. pH, T °C and CE measurements were done at the beginning and at the end of each experiment for all the samples.

### 2.5.1 Biochar

For each combination of water and biochar, four contact times were selected: 0.5, 2, 6, and 24 hours.

Before use, the biochar was hand ground with a pestle and mortar in order to reduce its size. Then, the fraction between 1.0 mm and 0.2 mm was selected using two sieves, allowing to separate the powder from the bigger fraction.

Since two repetitions were made for each water / biochar combination, eight samples were made and analysed for each contact times, using a total amount of 300 ml of each water and 6.0 g of each biochar.

During the mixing phase, biochar BC700 dispersed uniformly within both waters. On the contrary, biochar BC500 remained on the surface, especially at the beginning of the test. Furthermore, both biochars showed a greater affinity, i.e. greater miscibility, with wastewater ‘’Chiaro Flottatori’’, creating a homogeneous solution. In the case of wastewater “Chiaro Centrifughe”, biochar was often easily detectable floating on the surface. This difference in the solutions was more markedly visible in experiments with shorter contact times, while it tended to be smaller in longer contact times.

### 2.5.2 Activated carbon

In order to obtain a granulometric fraction similar to that of the biochar, the active carbon was in turn hand ground with a pestle and mortar. The fraction used for filtering tests was between 1.0 and 0.2 mm. For the combination activated carbon / wastewaters it was decided to use a contact time of two hours.

The activated carbon used as a comparison was produced by the company Carbotech DGK 8*30/60 from coconut shell. According to the data sheet of Carbotech the activated carbon should have a BET surface of about 1000m$^2$/g. However, further measurements at the University of Erlangen, Germany showed a BET surface (with Nitrogen) of only 756 m2/g.

### 2.5.3 Zeolite

The second material used for comparison was zeolite. Before it can be used, zeolite needs to be dried, in order to remove any humidity. Zeolite was dried in the oven at 100°C for 24 hours. 1.5 g of dry zeolites were put in each flask. For this combination, a total of 4 samples were made, i.e. two repetition for each wastewater.

The kinetic curve for zeolites was deducted from the data of a previous experiment[8], shown in Table 6. Based on this it was decided to use a 2-hour contact time for the filter test.

Table 6 – Concentration of $NH_4^-$ - N [mg] after zeolite treatment with different contact time (CT)

| **CT [min]** | **0** | **1** | **2** | **3** | **4** | **5** | **10** | **30** | **60** | **120** |
|---|---|---|---|---|---|---|---|---|---|---|
| **sand** | 78.8 | 72.2 | 68.8 | 65.5 | 65.0 | 61.6 | 57.5 | 51.6 | 43.2 | 38.2 |
| **powder** | 81.5 | 62.7 | 60.4 | 58.5 | 56.1 | 55.7 | 52.2 | 48.6 | 45.1 | 41.8 |

---

[8] J.P. Gutierrez, J. Bartel, Fraunhofer UMSICHT.

# 3 RESULTS

## 3.1 Characterization of feedstock, biochar and wastewater

Two biochars, used in the filtration tests, were produced from vine pruning at different post-reformer temperatures. The yields of the two different experiments, shown in Table 7, are in the expected range shown in Figure 1. The stucked feedstock refers to the amount of feedstock that, at the end of the experiment, was still in the hopper or in the pyrolysis chamber.

Table 7 - Biochar yield in g and % based on the feedstock that actually get pyrolyzed

| | Feedstock [g] | Stuck feedstock [g] | biochar yield [g] | biochar yield [%] |
|---|---|---|---|---|
| **BC700** | 1082 | 278 | 198 | 25% |
| **BC500** | 1431 | 484 | 282 | 30% |

The stuck feedstock refers to the amount of feedstock that, at the end of the experiment, was still in the hopper or in the pyrolysis chamber. The percentages of biochar compared to the initial feedstock were calculated not on the initial feedstock entered in the hopper but on the initial feedstock minus the stuck one.

### 3.1.1 Water and ash content

The water and ash content were measured for the feedstock and for the two produced biochar. The results are reported in Table 8.

Table 8 - water and ash content of feedstock, BC5700 and BC500

| | Water content | Ash content |
|---|---|---|
| **Feedstock** | 7% | 3% |
| **BC700** | 4% | 13% |
| **BC500** | 2% | 13% |

The ash content is greater in biochar than in feedstock because the ashes initially present in the feedstock concentrate in the solid pyrolysis products.

### 3.1.2 Calorific value

The calorific value of the two biochars and of the feedstock were measured. The results are reported in Table 9.

Table 9 - Calorific value measurements and average value for the feedstock and the biochars.

| | **Sample [g]** | **Measurements [J/g]** | **Average calorific value [J/g]** |
|---|---|---|---|
| **Feedstock** | 0.659 | 17469 | **17520** |
| | 0.656 | 17570 | |
| **BC700** | 0.680 | 28306 | **28305** |
| | 0.695 | 28304 | |
| **BC500** | 0.718 | 30783 | **30700** |
| | 0.680 | 30617 | |

Both biochars have a calorific value greater than the starting feedstock. In particular, the biochar BC700 shows an increase in the calorific value of 62% while the BC500 biochar shows an increase of 75%. The increase is due to the larger concentration of carbon in the biochar.

### 3.1.3 Biochar BET

The specific surface area, measured by the BET method, is shown in Table 10 for the two biochars. The results, expressed in $m^2/g$, show that the SSA of BC700 biochar is 56% higher than BC500.

Table 10 - SSA of biochar BC700 and BC500 measured with BET method

| | **CO2 - BET [$m^2/g$]** |
|---|---|
| **BC700** | 446 |
| **BC500** | 286 |

### 3.1.4 Elemental Analysis

Table 11 shows the content, in percentage, of N, C, H, S and O of both biochars and feedstock. The C content of both biochars is much higher compared to the feedstock, while the O and H content are lower and N and S content are equal.

Table 11 - Percentage content of N, C, H, S and O in feedstock, BC700 and BC500

| | N [%] | C [%] | H [%] | S [%] | O [%] |
|---|---|---|---|---|---|
| **FEEDSTOCK** | 0.79 | 45.60 | 6.69 | 0.04 | 46.88 |
| **BC700** | 1.07 | 80.77 | 0.95 | 0.09 | 17.12 |
| **BC500** | 1.27 | 85.86 | 2.55 | 0.08 | 10.24 |

### 3.1.5 Wastewater

The main parameters of the two wastewater samples supplied by Caviro EXTRA (see Figure 14) were measured before treatment. The results are shown in Table 12.

Figure 14 - Wastewaters samples provided by Caviro EXTRA

The pH of both waters was similar and slightly basic, settling around a value of 8. The content in orthophosphate ions and nitrate ions were also similar. The other parameters show differences between the two wastewaters, with greater values in the “Chiaro Centrifughe” water with respect to the “Chiaro Flottatori” water, except for the COD content.

Table 12 – Caviro EXTRA wastewaters characterization

| | | **Sample “Chiaro Centrifughe”** | **Sample “Chiaro Flottatori”** |
|---|---|---|---|
| **pH** | | 8.08 | 8.06 |
| **CE** | [mS/cm] | 11.4 | 13.6 |
| **COD** | [mg/l] | 471 | 419 |
| **$NO^{3-}$** | [mg/l] | 1.6 | 1.0 |
| **$NH_4$ -N** | [mg/l] | 679 | 987 |
| **$Cl^-$** | [mg/l] | 1250 | 1450 |
| **$PO_4^{3-}$ - P** | [mg/l] | 10.6 | 10.8 |

Wastewater dry matter content is shown in Table 13. The suspended solids present in both waste waters consist mostly of bacterial colonies released after the anaerobic digestion process from which these waters derive, and from the polyelectrolytes used to decrease the bacterial content of the wastewater.

Table 13 - Dry matter content in wastewaters express in g and wt%.

| | **Dry matter** | |
|---|---|---|
| | **g/L** | **% wt** |
| **Chiaro centrifughe** (unfiltered) | 5.94 | 0.60% |
| **Chiaro centrifughe** (filtered) | 5.84 | 0.58% |
| **Chiaro flottatori** (unfiltered) | 6.12 | 0.61% |
| **Chiaro flottatori** (filtered) | 6.00 | 0.60% |

## 3.2 Sorption tests

All the results of the sorption tests are shown in tables and in graphs. In the graphs, each measurement is represented with the associated standard error.

### 3.2.1 Results with Biochar

#### *Chlorine ions ($Cl^-$)*

Table 14 shows the $Cl^-$ content before and after sorption tests with biochar.

Table 14 - Wastewaters $Cl^-$ [mg/L] content before and after sorption with biochar.

| | | **Initial value** | **0.5h** | **2h** | **6h** | **24h** |
|---|---|---|---|---|---|---|
| **Chiaro Centrifughe** | BC700 | 1250 | 1400 | 1400 | 1000 | 1200 |
| | BC500 | | 1300 | 1300 | 1200 | 1000 |
| **Chiaro Flottatori** | BC700 | 1450 | 1300 | 1400 | 1200 | 1200 |
| | BC500 | | 1400 | 1300 | 1200 | 1100 |

Even if some variations in the content of chlorine ions in the waters are detected, it must be taken into account that, as explained in section 2.4.4, in order to be able to carry out the measurement it was necessary to dilute by 1:100 the samples. As a result, the measurement error is ±100 mg/L, thus making the differences not significant.

#### *Nitrogen ($NH_4^+$ - N)*

Table 15 shows the ammonium nitrogen content before and after sorption tests with biochar.

Table 15 - Variation of wastewaters $NH_4^+$ - N [mg/L] content before and after sorption with biochar.

| | | **Initial value** | **0.5h** | **2h** | **6h** | **24h** |
|---|---|---|---|---|---|---|
| **Chiaro Centrifughe** | BC700 | 679 | 746 | 781 | 671 | 726 |
| | BC500 | | 738 | 798 | 719 | 1149 |
| **Chiaro Flottatori** | BC700 | 987 | 1076 | 1081 | 968 | 986 |
| | BC500 | | 1045 | 1094 | 1041 | 1031 |

All the measured values for wastewater “Chiaro Centrifughe” are compatible with the initial value, except for the treatment with BC500 with a contact time of 24 hours, which shows an abnormally high result.

The results for the sample “Chiaro Centrifughe” are shown in Figure 15.

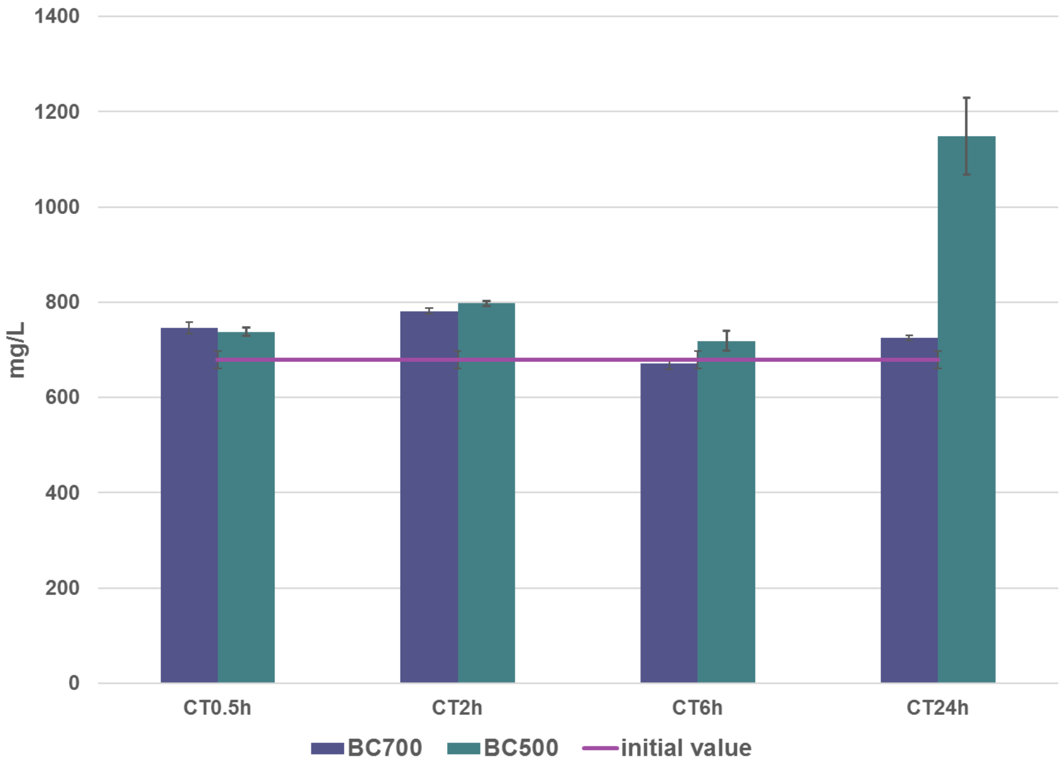


Figure 15 - $NH_4^+$ - N concentration after sorption with biochar in wastewater “Chiaro Centrifughe” compared with the initial value (purple line).

The results for sample “Chiaro Flottatori” are shown in Figure 16. The lowest value, of 968 mg/L, was measured for the treatment with BC700 and contact time of 6 hours.

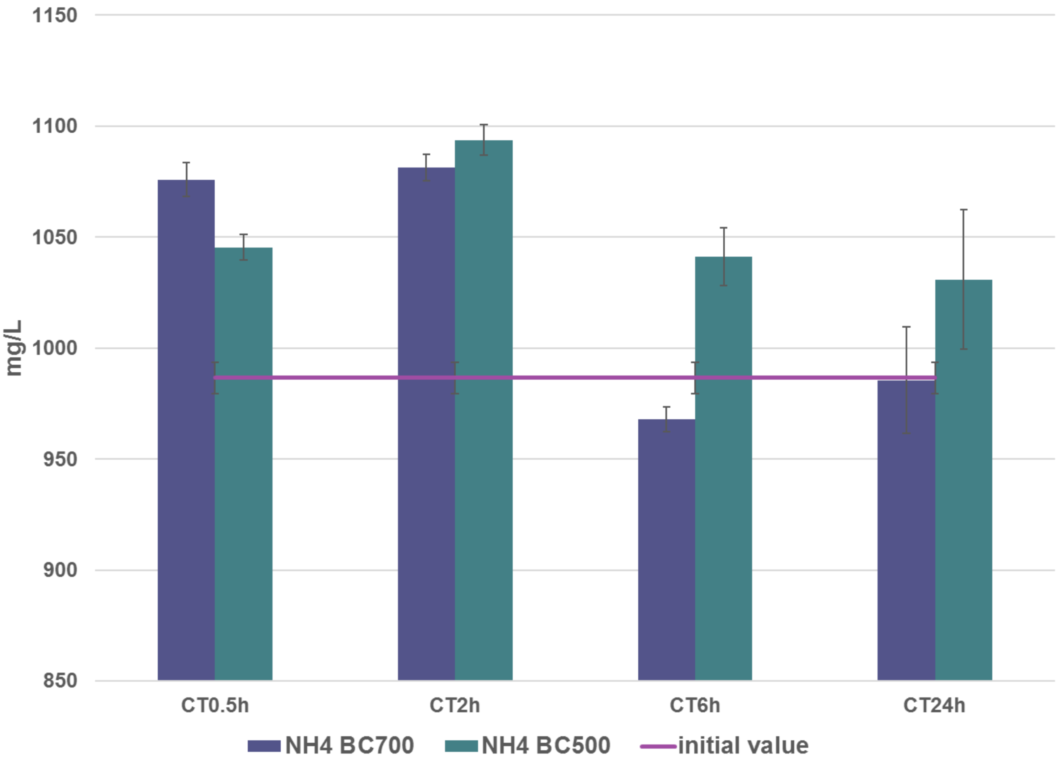


Figure 16 - NH4+ - N concentration after sorption with biochar in wastewater “Chiaro Flottatori” compared with the initial value (purple line).

In this case the ammonia content was reduced in two treatment with BC700, with contact time of 6 and 24 hours, while none of BC500 treatment gave a result lower than the initial value. However, in the BC700/24h treatment the difference between the initial value and the final one was inconsistent.

## *Phosphorous ($PO_4^{3-}$ - P)*

Table 16 shows the $PO_4^{3-}$ - P content before and after sorption tests with biochar.

Table 16 - Variation of wastewaters $PO_4^{3-}$ - P [mg/L] content before and after sorption with biochar.

| | | Initial | 0.5h | 2h | 6h | 24h |
|---|---|---|---|---|---|---|
| **Chiaro Centrifughe** | BC700 | 10.6 | 4.41 | 8.77 | 2.70 | 3.76 |
| | BC500 | | 3.58 | 7.25 | 4.06 | 2.76 |
| **Chiaro Flottatori** | BC700 | 10.8 | 4.27 | 8.86 | 7.55 | 7.45 |
| | BC500 | | 1.84 | 8.19 | 2.57 | 2.28 |

The results indicate a decrease in $PO_4^{3-}$ - P content with BC700 treatment. After half an hour the content significantly decreases, then it increases in the 2 hours contact time experiment and decreases again in the subsequent treatment, with contact time of 6 hours or more. A similar trend, but with a smaller reduction, is observed in the treatment with BC500.

A graphic representation of the phosphorus contents in both wastewaters after the different treatments with the two types of biochar is given in Figure 17 and Figure 18.

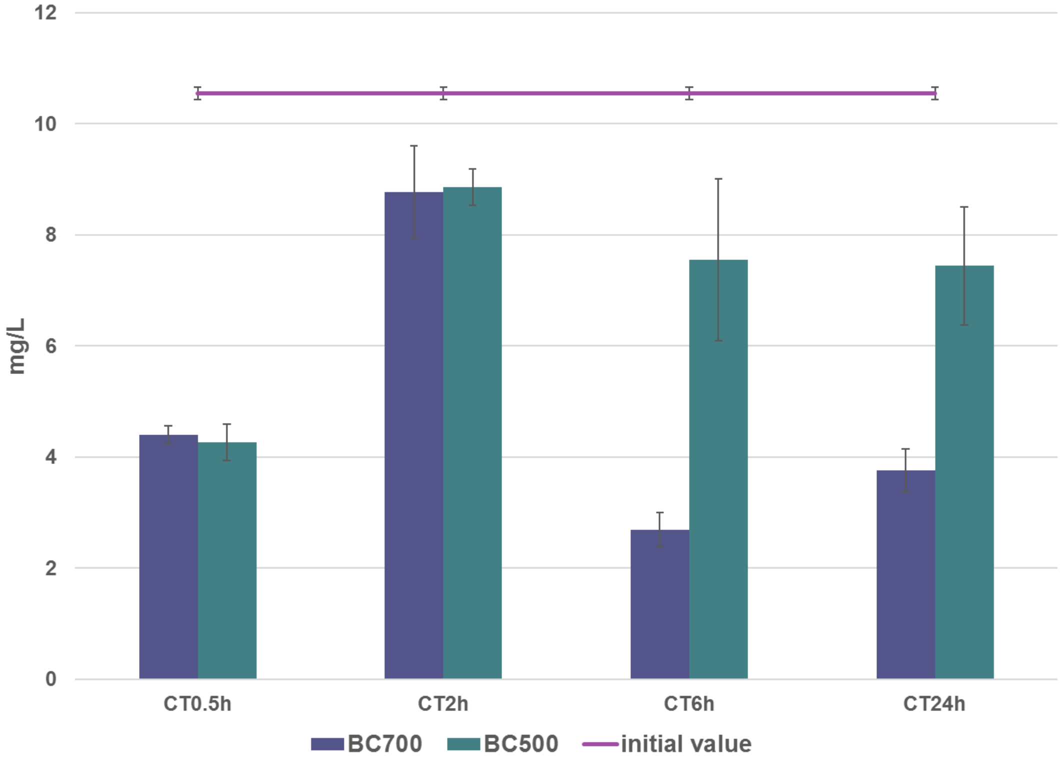


Figure 17 - $PO_4^{3-}$ - P concentration after sorption with biochar in wastewater “Chiaro Centrifughe” compared with the initial value (purple line).

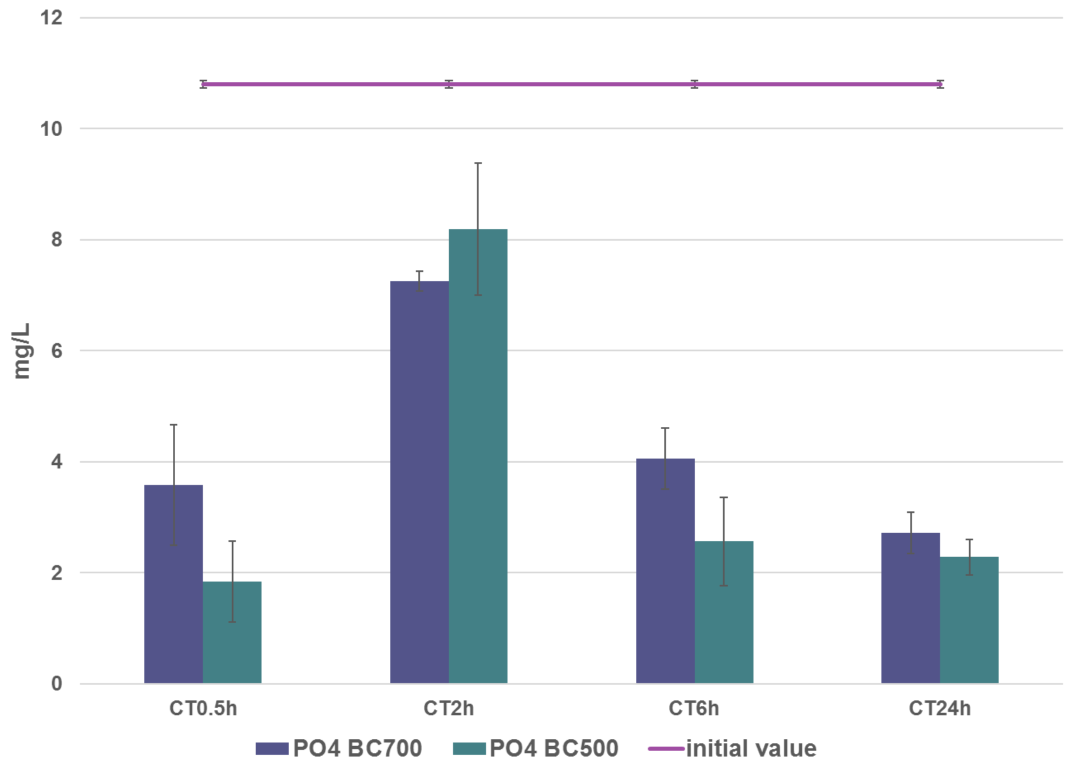


Figure 18 $PO_4^{3-}$ - P concentration after sorption with biochar in wastewater “Chiaro Flottatori” compared with the initial value (purple line).

## *COD*

The results obtained from the COD measurement are shown in Table 17.

Table 17 - Variation of wastewaters COD [mg/L] content before and after sorption with biochar

| | | **Initial** | **0.5h** | **2h** | **6h** | **24h** |
|---|---|---|---|---|---|---|
| **Chiaro Centrifughe** | BC700 | 470 | 278 | 290 | 241 | 285 |
| | BC500 | | 335 | 356 | 292 | 291 |
| **Chiaro Flottatori** | BC700 | 420 | 339 | 423 | 361 | 359 |
| | BC500 | | 404 | 384 | 380 | 389 |

All COD values measured after sorption with biochar are lower than the initial value for both wastewaters. In the case of sample “Chiaro Flottatori” the greatest reduction was obtained with BC700 treatment and 6 hours contact time. The smallest reduction compared with the initial value was obtained with BC500 and 2 hours contact time.

The results for the two wastewater samples are shown in Figure 19 and Figure 20, respectively. The wastewater sample “Chiaro Flottatori” shows the larger effect.

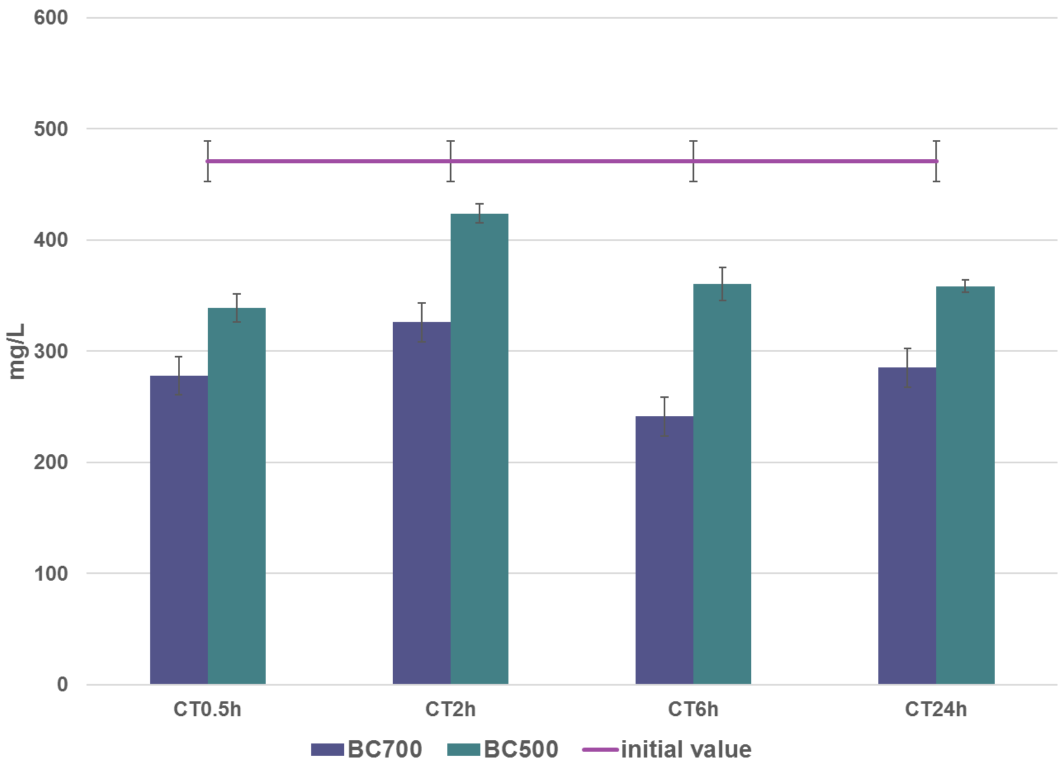


Figure 19 - COD concentration between treatments in wastewater “Chiaro Centrifughe” compared with the initial value (purple line).

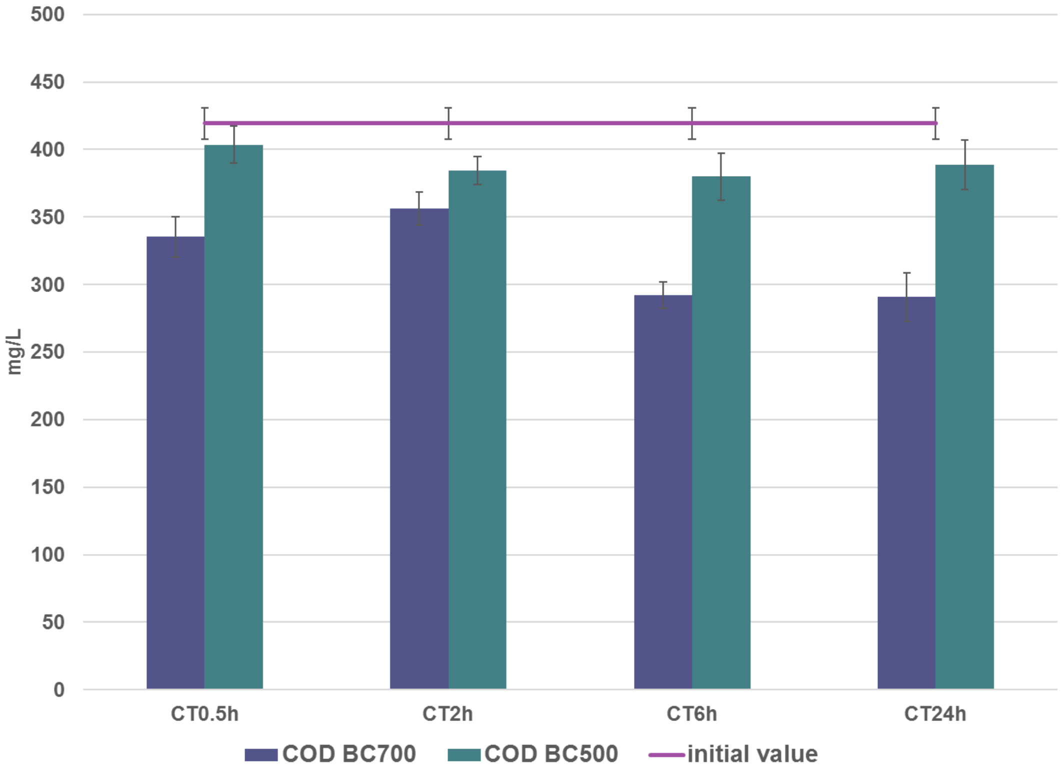


Figure 20 - COD concentration between treatments in wastewater “Chiaro Flottatori” compared with the initial value (purple line).

### 3.2.2 Results with Activated Carbon

The sorption test with Activated Carbon (AC) was performed only with contact time of two hours. The results are shown in Table 18. The graphic representations are reported in Figure 21 and Figure 22.

Table 18 - Wastewaters characterization after sorption with AC, initial and after 2h contact time

| | **COD [mg/L]** | | **$NH_4^+$ - N [mg/L]** | | **$PO_4^{3-}$ - P [mg/L]** | |
|---|---|---|---|---|---|---|
| | **initial value** | **2h** | **initial value** | **2h** | **initial value** | **2h** |
| **“Chiaro centrifughe”** | 470 | 379 | 679 | 790 | 679 | 790 |
| **“Chiaro flottatori”** | 420 | 373 | 987 | 1033 | 987 | 1033 |

## *Nitrogen ($NH_4^+$ - N)*

The activated carbon was not effective in the removal of ammonium. In none of the two wastewater samples there was a reduction in ammonium detected.

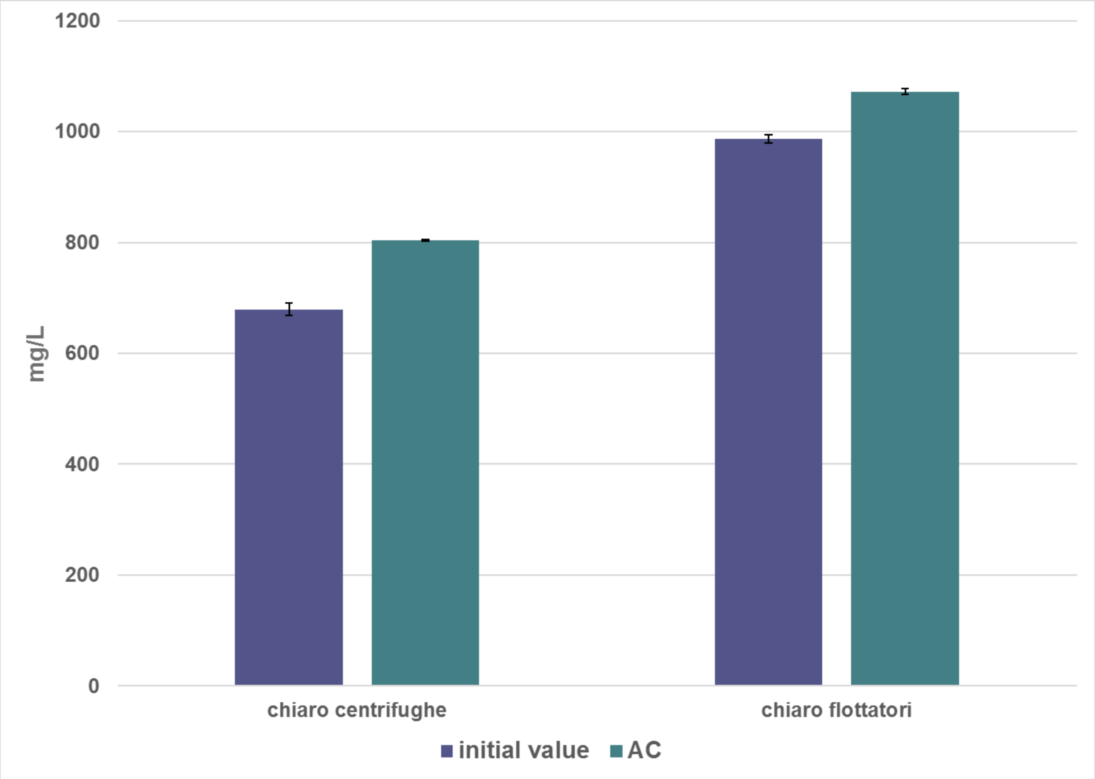


Figure 21 - $NH_4^+$ - N concentration in wastewaters after AC treatment compared with the initial value

## *Phosphorous ($PO_4^{3-}$ - P)*

Activated carbon performance in removing P from wastewater was not very effective. Some reduction happened in wastewater “Chiaro Flottatori”, but the difference with the initial value was very low. In wastewater “Chiaro Centrifughe” no reduction was detected (see Figure 22).

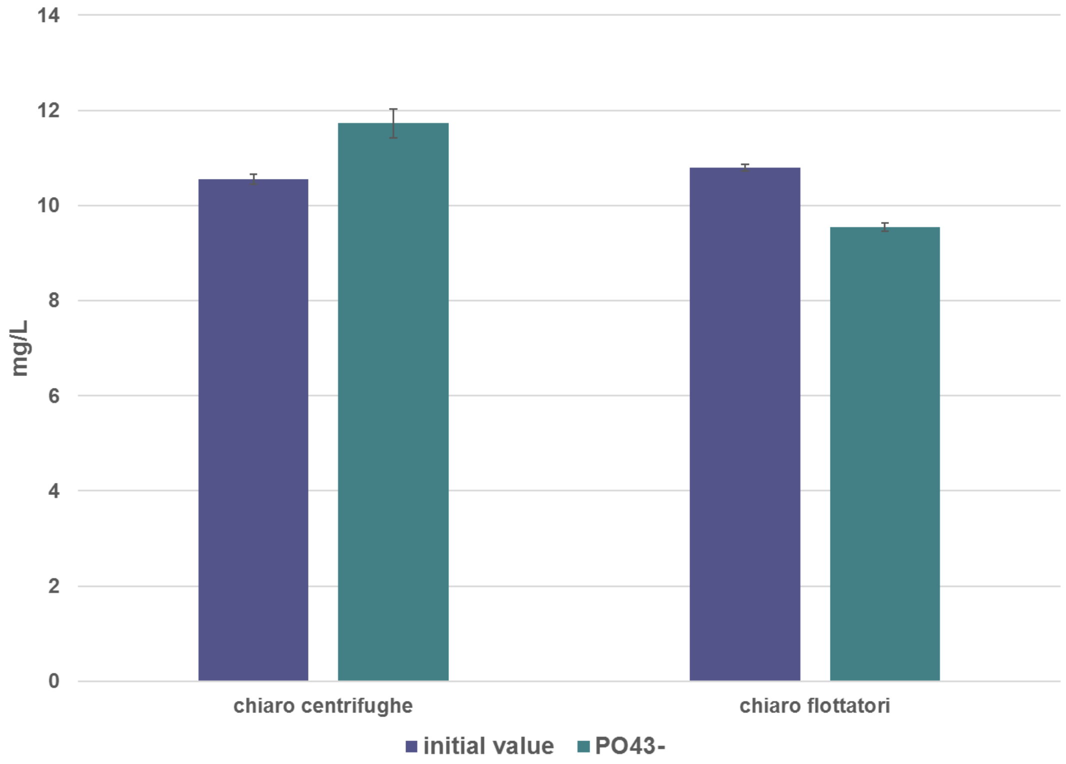


Figure 22 - $PO_4^{3-}$ - P concentration in wastewaters after AC treatment compared with the initial value

## COD

Activated carbon has proved effective in reducing COD in both waters. In the "Chiaro Centrifughe" sample the reduction was, as in the case of both biochars, greater than in the "Chiaro Flottatori" sample. The reduction in the two samples was 30% and 8% respectively.

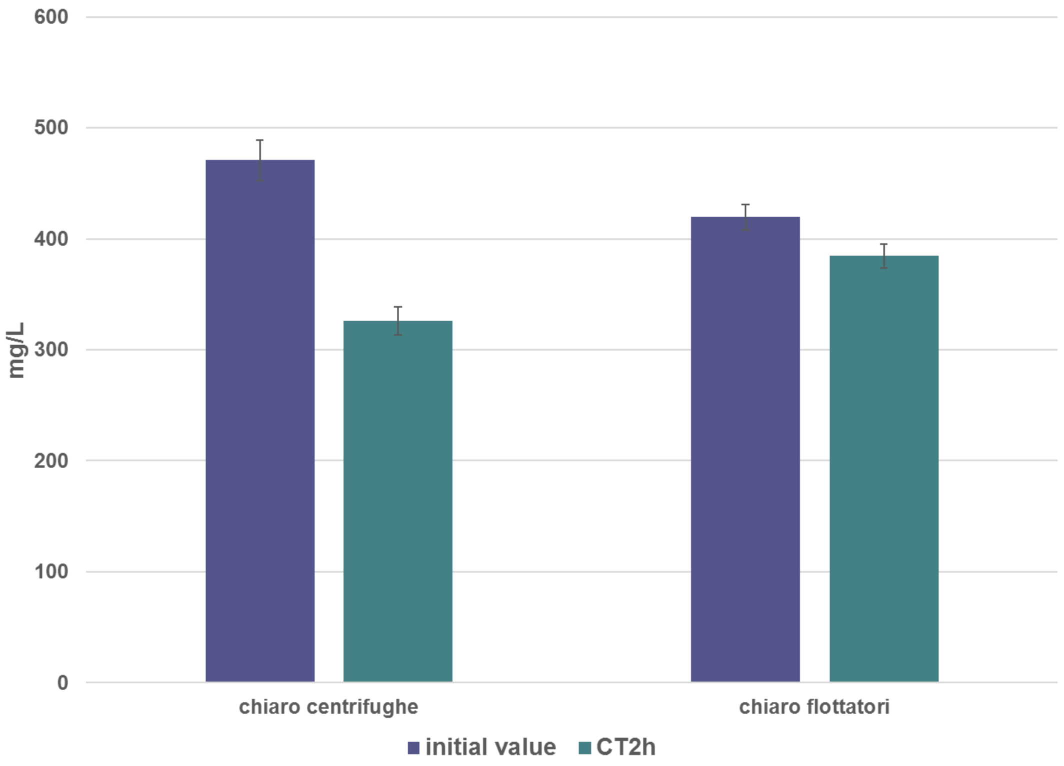


Figure 23 - COD concentration in wastewaters after AC treatment compared with the initial value

### 3.2.3 Results with Zeolites

Zeolites have been used mainly as a comparison for the reduction of $NH_4^+$ in the wastewater, but since they have more general absorbing properties, the reduction of COD was also measured. The $NH_4^+$ and COD values detected after treatment are shown in Table 19.

Table 19 - Wastewaters characterization after Zeolite treatment, 2h contact time

| | **COD [mg/L]** | | **$NH_4^+$ - N [mg/L]** | |
|---|---|---|---|---|
| | **initial value** | **2h** | **initial value** | **2h** |
| **"Chiaro centrifughe"** | 470 | 379 | 679 | 790 |
| **"Chiaro flottatori"** | 420 | 373 | 987 | 1033 |

## *Nitrogen ($NH_4^+$ - N)*

Although zeolites were supposed to have a better capacity of reducing ammonium with respect to biochar, the results are negative in both wastewater samples, as shown in Figure 24.

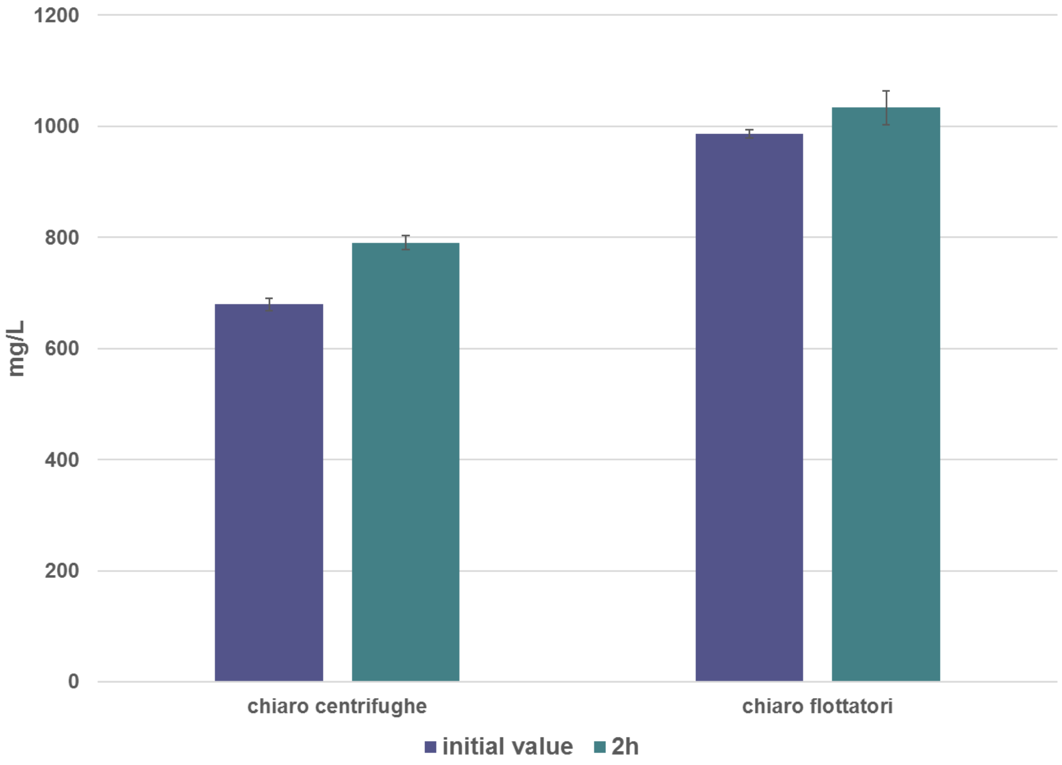


Figure 24 - $NH_4^+$ - N concentration in wastewaters after Zeolite treatment compared with the initial value

With neither of the two waste waters the zeolites were able to reduce the COD content and a recurrence of ammoniacal nitrogen was recorded in both cases.

### *COD*

The COD (Figure 25) was reduced in both waters arriving at values very similar to each other. The wastewater sample "Chiaro Centrifughe" shows the greater reduction at about 20%. The reduction in the wastewater sample "Chiaro Flottatori" is slightly more than 10%.

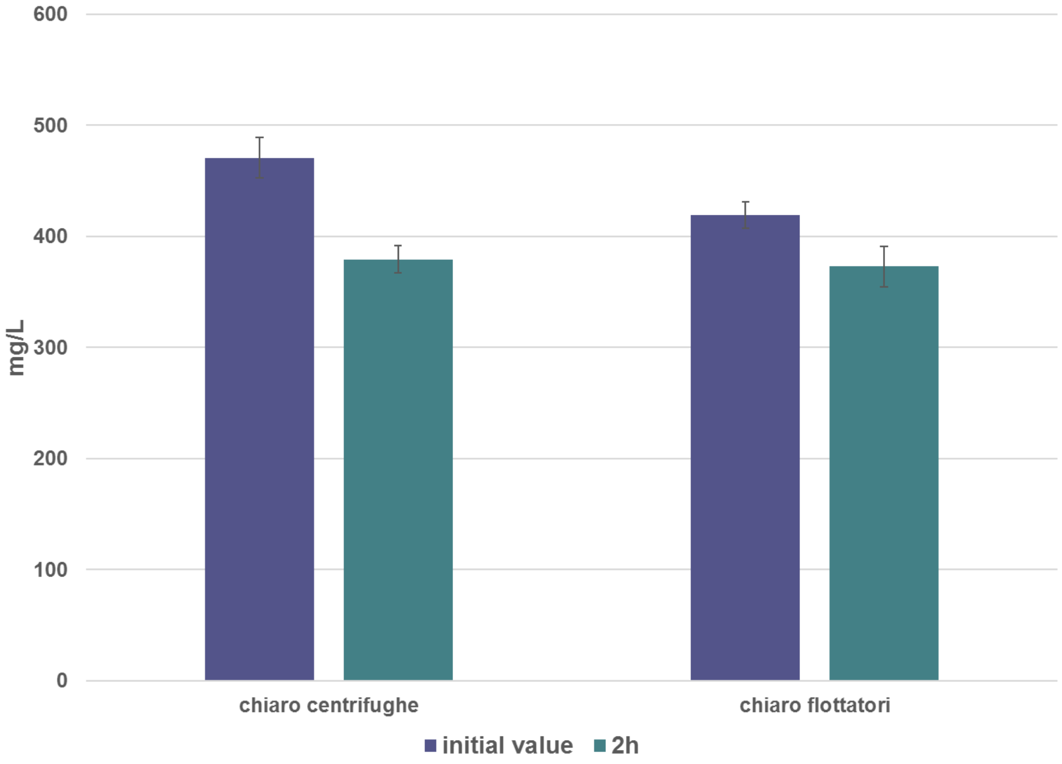


Figure 25 - COD concentration in wastewaters after Zeolite treatment compared with the initial value

## 3.3 Economic assessment

The search for filter materials with a competitive price compared to activated carbon has led to the study of biochar as a filter material. According to IBI reports in 2014, the average retail price for pure biochar is 3.08 USD/kg.[9] According to the literature, the average price for activate carbon is 5.60 USD/kg (Alhashimi & Aktas, 2017).

In the following, the calculation of the cost of the filtering material as a function of the reduction capacity on main pollutants will be illustrated, following the results of the experiments given in section 3.2. These costs will be compared to the cost of disposing the wastewater without treatment, according to the tariffs applied in the Emilia-Romagna Region.

The four main parameters involved in wastewater treatment are COD, TSS, Phosphorous and Nitrogen content. However, since the effect of biochar on TSS was not measured and the content of N in the wastewater did not decrease after sorption, only COD and Phosphorous are considered in the following.

The percentage reduction of COD from the two wastewaters obtained with biochar treatment is shown in Table 20.

Table 20 - Percentage reduction of COD in the two waste waters in the different treatments with **biochar**

| | | CT 0.5h | CT 2h | CT 6h | CT 24h |
|---|---|---|---|---|---|
| **Chiaro Centrifughe** | **BC700** | -41% | -38% | -49% | -39% |
| | **BC500** | -29% | -10% | -38% | -38% |
| **Chiaro Flottatori** | **BC700** | -20% | -15% | -30% | -31% |
| | **BC500** | -4% | -8% | -9% | -7% |

The quantity of reduced COD per gram of filtering material is shown in Table 21 for wastewater “Chiaro Centrifughe” and Table 22 for wastewater “Chiaro Flottatori”.

---

[9] https://biochar-international.org/state-of-the-biochar-industry-2014/

Table 21 - Quantity of COD removed per gram of filter material in “Chiaro Centrifughe” wastewater

| Contact time | $g_{COD}/g_{BC700}$ | $g_{COD}/g_{BC500}$ | $g_{COD}/g_{AC}$ | $g_{COD}/g_{Zeolites}$ |
|---|---|---|---|---|
| **0.5h** | 12.852 | 8.790 | - | - |
| **2h** | 12.041 | 3.126 | 9.663 | 6.093 |
| **6h** | 15.300 | 7.349 | - | - |
| **24h** | 12.372 | 7.477 | - | - |

Table 22 - Quantity of COD removed per gram of filter material in “Chiaro Flottatori” wastewater

| Contact time | $g_{COD}/g_{BC700}$ | $g_{COD}/g_{BC500}$ | $g_{COD}/g_{AC}$ | $g_{COD}/g_{Zeolites}$ |
|---|---|---|---|---|
| **0.5h** | 5.606 | 1.055 | - | - |
| **2h** | 4.210 | 2.343 | 2.321 | 3.106 |
| **6h** | 8.474 | 2.620 | - | - |
| **24h** | 8.581 | 2.038 | - | - |

The experiment showed that to reduce the COD content of wastewater “Chiaro Centrifughe” by 49%, 1.5 g of BC were required, with a contact time of 6h (see Table 20). The needed quantity of AC and Zeolite for the same reduction are, respectively, 2.4 g, with an AC:WASTEWATER ratio of 1:30, and 3.8 g, with a Zeolite:WATEWATER ratio of 1:20.

For wastewater “Chiaro Flottatori” the maximum COD decrease (31%) occurred after 24 hours with the BC700 biochar. To obtain the same effect, 5.5 g of AC would be necessary, with an AC: WASTEWATER ratio of 1:13, and 4.1 g of zeolite, with a ratio of 1:18.

As mentioned in chapter 2.3.1, $2.15 \times 10^8$ L of “Chiaro Centrifughe” wastewater and $5.55 \times 10^8$ L of “Chiaro Flottatori” are produced each year. To get the maximum reduction of COD in “Chiaro Centrifughe” wastewater, with a ratio of BC:WASTEWATER of 1:50 a total of $1.11 \times 10^7$ kg of biochar would be needed. To obtain the same results with activated carbon, $1.85 \times 10^8$ kg would be needed. Given the average cost of 3.08 USD/kg for biochar and 5.60 USD/kg for activated carbon, an investment of $3.42 \times 10^7$ USD/year with biochar will be required, 67% less than activated carbon, whose investment would be $1.0 \times 10^8$ USD/year. For Zeolite, the investment would be $2 \times 10^9$ USD/year.

Likewise, for “Chiaro Flottatori” wastewater, the investment for AC and Zeolites would be respectively $9 \times 10^7$ and $1 \times 10^9$ USD/year, compared with $1.3 \times 10^7$ USD/year for biochar.

The total savings for both wastewaters, resulting from the replacement of activated carbon with biochar, would be 75%. The replacement of zeolite with biochar, would save 80% of the cost.

The calculation of how many grams of COD are removed as a function of porosity have also been done, as shown in Table 23 and Table 24. As stated in chapter 2.5.2, the declared porosity of the activated carbon and the one actually measured were different, so the ratio was calculated for both declared and measured SSA.

Table 23 - Quantity of COD removed per $m^2$ of filter material in “Chiaro Centrifughe” wastewater

| **Contact time** | $g_{COD}/m^2_{BC700}$ | $g_{COD}/m^2_{BC500}$ | $g_{COD}/m^2_{AC}$ | $g_{COD}/m^2_{AC\_bis}$ |
|---|---|---|---|---|
| **0.5h** | 0.043 | 0.046 | - | - |
| **2h** | 0.040 | 0.016 | 0.014 | 0.019 |
| **6h** | 0.051 | 0.039 | - | - |
| **24h** | 0.042 | 0.039 | - | - |

Table 24 - Quantity of COD removed per $m^2$ of filter material in “Chiaro Flottatori” wastewater

| **Contact time** | $g_{COD}/m^2_{BC700}$ | $g_{COD}/m^2_{BC500}$ | $g_{COD}/m^2_{AC}$ | $g_{COD}/m^2_{AC\_bis}$ |
|---|---|---|---|---|
| **0.5h** | 0.019 | 0.006 | - | - |
| **2h** | 0.014 | 0.012 | 0.003 | 0.005 |
| **6h** | 0.028 | 0.014 | - | - |
| **24h** | 0.029 | 0.011 | - | - |

The amount of phosphorus also decreased after the treatment with biochar, while no changes were observed with activated carbon. The ratios of removed phosphorus and biochar needed are shown in Table 25 for waste water “Chiaro Centrifughe” and in Table 26 for waste water “Chiaro Flottatori”.

Table 25 - Quantity of P removed per gram of filter material in “Chiaro Centrifughe” wastewater

| **Contact time** | $g_P/g_{BC700}$ | $g_P/g_{BC500}$ | $g_P/g_{AC}$ |
|---|---|---|---|
| **0.5h** | 0.413 | 0.422 | - |
| **2h** | 0.122 | 0.116 | - |
| **6h** | 0.527 | 0.203 | - |
| **24h** | 0.456 | 0.210 | - |

Table 26 - Quantity of P removed per gram of filter material in “Chiaro Flottatori” wastewater

| Contact time | $g_P/g_{BC700}$ | $g_P/g_{BC500}$ | $g_P/g_{AC}$ |
|---|---|---|---|
| **0.5h** | 0.481 | 0.597 | - |
| **2h** | 0.236 | 0.174 | 0.084 |
| **6h** | 0.449 | 0.549 | - |
| **24h** | 0.539 | 0.568 | - |

The calculation of removed phosphorus with respect to the biochar surface leads to a very low value, of the order of 0.001 g/m$^2$ in each treatment.

Although the amount of P per litre of wastewater is low (1.07 g/L), the 7.7x10$^8$ L/year of wastewater produced by CAVIRO Extra contain 8.24x10$^5$ kg of phosphorus, a quite high amount.

The biochar filtering method applied to industrial wastewater represents an economic saving compared both to filtering with AC and to water purification as explained in the following.

On December 21, 2018, the EMILIA-ROMAGNA TERRITORIAL AGENCY FOR WATER AND WASTE SERVICES approved the “Testo Integrato Corrispettivi Servizi Idrici (TICSI), recante i criteri di articolazione tariffaria applicata agli utenti", i.e. the new tariff structure in the territory of the province of Bologna (Delibera ARERA n. 665/2017/R/IDR).

The cost of collecting and purifying industrial wastewater that is authorized to be dumped into the public sewer is calculated according to the following formula:

$$T = QF + QC + QV + V$$

where:

- QF represents a fixed quota in Euro/year;
- QC is the capacity quota, linked to the purification capacity used to guarantee the treatment of industrial wastewater from the industrial user (Euro/year);
- QV is the variable quota, depending on the volume and quality of the dumped wastewater (Euro/m$^3$);
- V is the annual volume dumped (m$^3$/year).

The QF quota being fixed is not influenced either by the quantity or by the quality of the wastewater to be treated. On the contrary, the QV quota is strictly dependent on the quality of the wastewater. Four main pollutants, COD, SST, N and P are considered in the computation of QV, following the formula:

$$QV = Tf + max\{1; q\} \cdot Td$$

Where:

$$q = \left[W_{COD} \cdot \frac{COD}{COD_{rif}} + W_{SST} \cdot \frac{SST}{SST_{rif}} + W \cdot \frac{N}{N_{rif}} + W_P \cdot \frac{P}{P_{rif}} + + \sum_j W_{X,j} \cdot \frac{X_j}{X_{j,rif}}\right]$$

- T*f* eT*d* rates are determined annually. T*f* means “tariffa unitaria di fognatura”, i.e. unite rate of sewerage. T*d*, “tariffa quali-quantitativa di depurazione”, is a qualitative-quantitative purification unit rate. Both T*f* and T*d* are measured in €/m$^3$.
- COD, TSS, N and P represent the initial concentrations of the main pollutants in the wastewater dumped by the industrial user (mg/L).
- $COD_{rif}$, $SST_{rif}$, $N_{rif}$ and $P_{rif}$ represent the concentrations of the four main pollutants in the reference wastewater. Their value (reported in Table 27) is equal to the discharge limits in surface water bodies for industrial waste referred to in Table 3, column "Discharge in surface waters", of Annex 5 to Part Three of Legislative Decree 152/2006 and amendments, for sensitive areas.

The *W*s represent the standard weight of each pollutant in the final cost evaluation (

- Table 28).

Table 27 - Reference value for the main pollutants

| Parameter | Value [mg/L] |
|---|---|
| **$COD_{rif}$** | 160 |
| **$SST_{rif}$** | 80 |
| **$N_{rif}$** | 10 |
| **$P_{rif}$** | 1 |

Table 28 - Standard weight values for main pollutants

| **Parameter** | **Value [%]** |
|---|---|
| $W_{COD}$ | 52 |
| $W_{SST}$ | 28 |
| $W_{N}$ | 15 |
| $W_{P}$ | 5 |

- X and $W_X$ are respectively the concentration and the percentage value of any additional specific pollutants present in the wastewater (mg/L).

Applying the formula to the thesis case study, the parameters to be taken into consideration are those relating to COD, N and P. Looking at the formula and at

Table 28 it can be seen that more than 50% of the contribution to the value of QV is given by the COD.

Tables 29 and 30 show the *q* values calculated for each treatment and for each filtering material. The two tables refer to wastewater “chiaro centrifughe” and “chiaro flottatori” respectively.

Table 29 – Calculation of the *q* values for “Chiaro Centrifughe” wastewater

| | Initial value | 0.5h | 2h | 6h | 24h |
|---|---|---|---|---|---|
| **Zeolites** | 1.53 | - | 1.28 | - | - |
| **AC** | 1.53 | - | 1.65 | - | - |
| **BC500** | 1.53 | 1.32 | 1.82 | 1.55 | 1.54 |
| **BC700** | 1.53 | 1.12 | 1.38 | 0.92 | 1.12 |

As can be seen for wastewater “chiaro centrifughe” the value of q less is obtained in correspondence with the treatment with BC700 and contact time of 6h. The higher value is obtained in correspondence with the treatment with BC500 for 2h.

Table 30 - Calculation of the *q* values for “Chiaro Flottatori” wastewater

| | Initial value | 0.5h | 2h | 6h | 24h |
|---|---|---|---|---|---|
| **Zeolites** | 1.36 | - | 1.26 | - | - |
| **AC** | 1.36 | - | 1.25 | - | - |
| **BC500** | 1.36 | 1.40 | 1.66 | 1.36 | 1.38 |
| **BC700** | 1.36 | 1.27 | 1.52 | 1.15 | 1.08 |

In the case of wastewater “chiaro flottatori” the optimal value of q is obtained with the BC700 treatment and contact time of 24h, while the highest with BC500 and 2 hour contact time.

QV values in €/m$^3$ and € have been calculated by applying QV formula. T*f* and T*d* values are reported in Table 31. QV have been calculated for every filter material, using COD and P value from the treatments with the best performances.

Table 31 – Td, Tf and wastewaters volume values.

| Td [€/m$^3$] | Tf [€/m$^3$] | Chiaro Centrifughe [L] | Chiaro Flottatori [L] |
|---|---|---|---|
| 0.519 | 0.209 | $5.55 \times 10^8$ | $2.15 \times 10^8$ |

QV values for wastewater “Chiaro Centrifughe” are reported in Table 32. QV was calculated using the best case, i.e. with the best performance of the filtering material, for each material.

Table 32 - Values of QV for wastewater “Chiaro Centrifughe” in the various treatments (best cases)

| | **INITIAL** | **BC700** | **BC500** | **AC** | **Zeolites** |
|---|---|---|---|---|---|
| **QV** [€/m3] | 1.00 | 0.73 | 0.89 | 1.06 | 0.87 |
| **QV** [€] | $5.57x10^8$ | $4.04x10^8$ | $4.95x10^8$ | $5.9x10^8$ | $4.86x10^8$ |

As already seen before, in the case of wastewater “Chiaro Centrifughe” the greatest saving is achieved when water is treated with BC700. The QV value in this case is 0.73 €/m$^3$, against 1 €/m$^3$ for untreated water. In this case, with the exception of the treatment with activated carbon, all the treatments are advantageous. The best case economic savings in € and % with respect to un filtered wastewaters with all filtering methods are shown in Table 33.

Table 33 - Economic savings with all filtering methods (best cases) for “Chiaro Centrifughe” wastewater

| | **BC700** | **BC500** | **AC** | **Zeolites** |
|---|---|---|---|---|
| **Economic saving** [%] | 27% | 11% | - | 13% |
| **Economic saving** [€] | $1.53x10^8$ | $6.20x10^7$ | - | $7.12x10^7$ |

The worst treatment turns out to be that with activated carbon which not only does not entail an economic saving, but actually increases the cost of water disposal.

Also with “Chiaro Flottatori” wastewater, the best treatment is with BC700. In this case BC500 has the worst performance, not giving any savings. The treatments with activated carbon and zeolites have the same effect.

Table 34 - Values of QV for wastewater “Chiaro Flottatori” in the various treatments (best cases)

| | INITIAL | BC700 | BC500 | AC | Zeolites |
|---|---|---|---|---|---|
| **QV** [€/m3] | 0.92 | 0.77 | 0.92 | 0.86 | 0.86 |
| **QV** [€] | $1.97 \times 10^8$ | $1.66 \times 10^8$ | $1.97 \times 10^8$ | $1.84 \times 10^8$ | $1.86 \times 10^8$ |

The economic savings in % and € for wastewater “Chiaro Flottatori” are shown in Table 35.

Table 35 - Economic savings with all filtering methods (best cases) for “Chiaro Flottatori” wastewater

| | BC700 | BC500 | AC | Zeolites |
|---|---|---|---|---|
| **Economic saving** [%] | 16% | - | 6% | 6% |
| **Economic saving** [€] | $3.16 \times 10^7$ | - | $1.26 \times 10^7$ | $1.13 \times 10^7$ |

The cost of purchasing the char has to be subtracted from the saving. The net savings are shown in the Table 36 for the BC700 treatment case. For the other treatments there would be no economic saving, due to the cost of the filter material.

Table 36 - Net economic saving using BC700 treatment

| | Chiaro Centrifughe | Chiaro Flottatori | Total saving |
|---|---|---|---|
| **Net economic saving** [€] | $1.19 \times 10^8$ | $1.8 \times 10^7$ | $1.37 \times 10^8$ |

The savings could increase if the biochar, once used as a filtering material, was resold as a fertilizer. In every scenario, cost derived from filtering plant and management are not considered.

# 4 DISCUSSION

## 4.1 Biochar production and wastewater filtration with biochar

The two biochars produced with the TCR technology have proved to be very different both for their characteristics and for their performance as filtering materials.

As described in the previous chapter, the parameters that have been measured after the filtration tests are COD, ammonia nitrogen, ortho-phosphate phosphorus and chloride. It has been chosen not to measure nitrate nitrogen since the concentration in the untreated wastewaters was very low and close to the detection limit of the instruments.

The most interesting results are those concerning COD, ammonia and phosphorus, since chloride did not show any change in values. The BC700 biochar proved to be particularly effective, compared to the BC500 biochar, in reducing the COD content in both waters, achieving a 50% reduction in the "Chiaro Centrifughe" wastewater sample. In contrast, the BC500 biochar proved to be less effective, although there was a reduction in COD. These results are coherent with the literature about COD reduction with biochar (Barber, Yin, Draper, & Trabold, 2018b; Huggins et al., 2016; Sun et al., 2018).

For both the combination wastewater / biochar the difference between the COD initial value of and the values after the sorption tests are substantial.

As for ammonium, neither of the biochars proved effective in reducing it. This may be due to interference occurring during the experiments between the biochar, the wastewater and the suspended solids it contains. As previously mentioned, the waters used in this thesis are real process waters, and not synthetic waters. Both waters derive from anaerobic digestion processes, so that there are still bacterial colonies which, at room temperature, could began their cycle again, using and producing substances, potentially including ammonium. This interpretation is supported by the fact that not even the commercial Activated Carbon and Zeolites filter materials have been proved effective in reducing the amount of ammonium.

Another interpretation is that the solids present inside the waters have physically interfered with biochar, sticking to its surface and thus blocking the sites that could have absorbed ammonium, thus preventing water from entering into contact with some of the pores, especially those more internal to the biochar structure, effectively limiting ammonium sorption. This same effect could have interfered on the removal of other monitored compounds. It is therefore legitimate to think that even the reduction of the COD has been, for example, limited.

Regarding the reduction of phosphate, the performances were extremely different. As already mentioned in chapter 3, in the case of the sample "Chiaro Centrifughe" the biochar BC700 had a greater effectiveness in its reduction, especially with contact times greater than six hours. On the contrary, in the case of the "Chiaro Flottatori" sample, it was the BC500 biochar that was more effective, even after only half an hour. Although other experiments have used biochar to remove phosphate from water, these strong differences between the two wastewaters can be an indication that something else is happening. Given the complexity of the system under examination it is difficult to attribute the reduction completely to biochar. From the previously reported results it is possible to note that, after the treatments, pH variations have occurred, which may have caused the precipitation of the phosphorus as a solid phase.

Reduction of P in wastewater normally occurs with Mg impregnated biochar. This is necessary because biochar surface is often negatively charged, which prevent its interaction with other negatively charged compounds, as $PO_4^{3-}$ (Yi & Chen, 2018). Even if the biochar produced for these experiments was not loaded with Mg, it is possible that Mg was naturally present in the biochar, leading to a P reduction in the wastewaters. Another explanation could be that P precipitated as struvite (magnesium ammonium phosphate), but since no ammonium decrease was detected, the mechanism is unlikely to have occurred (Stratful, Scrimshaw, & Lester, 2001).

The different behaviour of the two biochars as filtering materials is most probably to be attributed to the strong difference in their SSA, and therefore to the different temperature of the post-reformer, during the production phase, which determined it (Stenzel et al., 2016).

## 4.2 Comparison between biochar, activated carbon and zeolite filter

The performance in the reduction of COD of activated carbon and zeolite were compared, with the same contact time, with the results obtained from the treatment of wastewater with the two biochars. In turn, all the results are compared with the initial COD value. A summary of the results is shown in Figure 26.

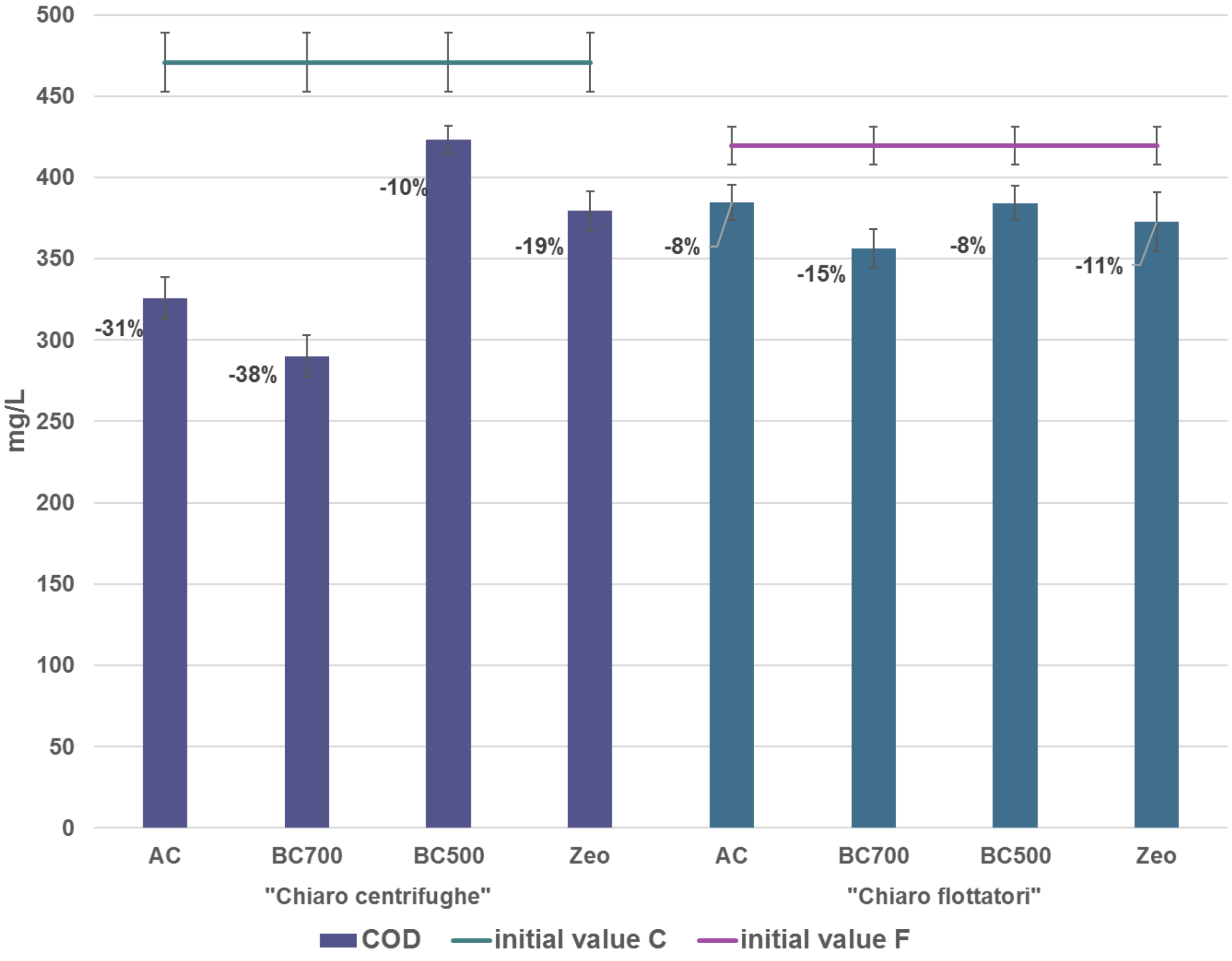


Figure 26 - Comparison in COD removal performance between AC, BC700, BC500 and Zeolite and with the initial value.

The reduction of COD was more effective in the case of “Chiaro Centrifughe” wastewater. In fact, with water “Chiaro Flottatori” the maximum reduction is 15% for the longer contact times. In both cases the best performance is that of biochar BC700.

Moreover, biochar performances were even better in treatment with different contact times. In graph below (Figure 27) the results obtained with activated carbon and zeolites are compared with the best results obtained with BC700 and BC500.

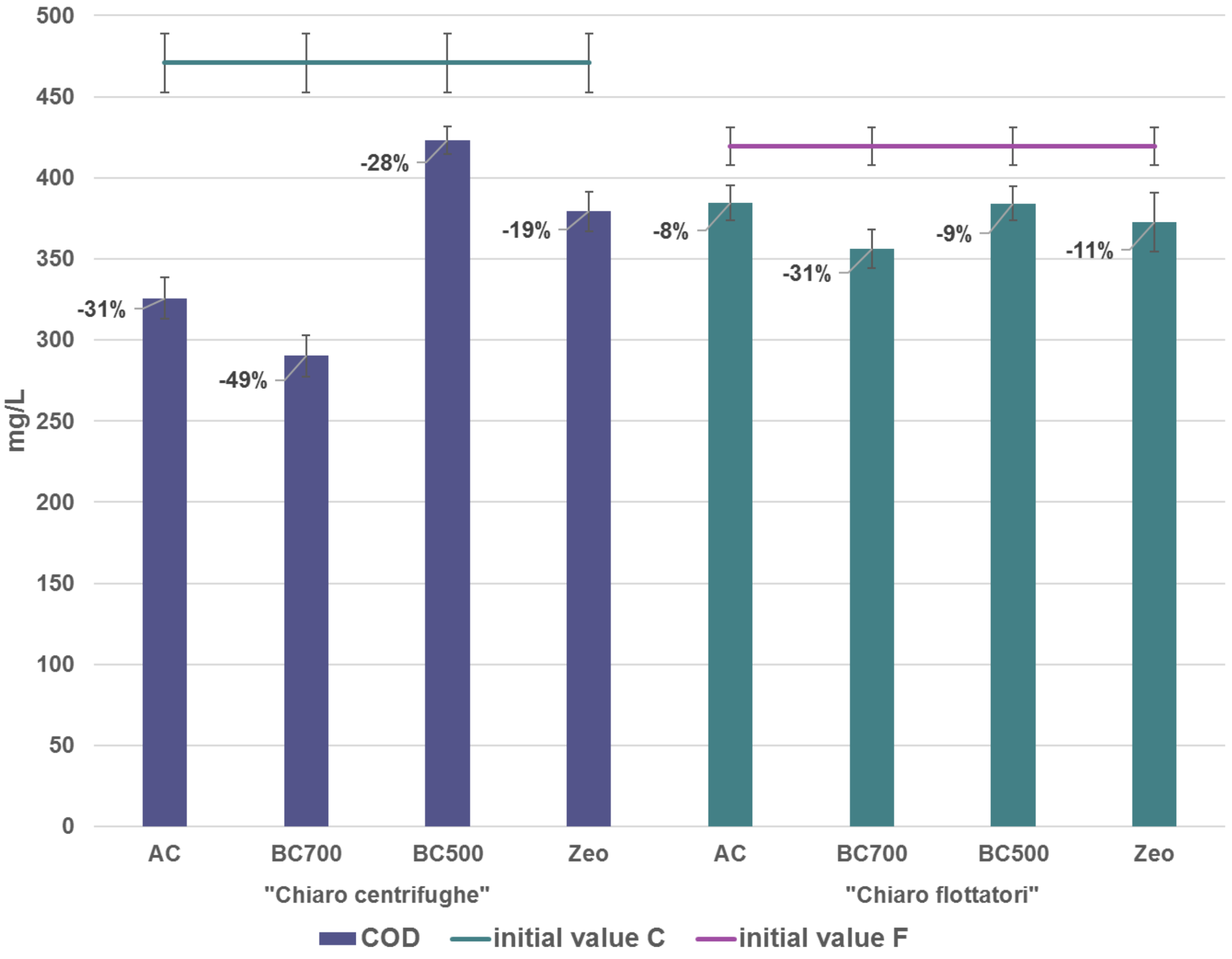


Figure 27 - Comparison in COD removal performance between AC, BC700, BC500 and Zeolite and with the initial value (best cases).

The BC700 proved to be the best filtering material in all cases, unlike the BC500 which always had worse performance or, in the best case, the same as other materials.

As shown in chapter 3, no filter media used in this thesis was able to reduce the amount of N in the two wastewaters. The reason behind this result probably lies in the initial composition of the two waters. As previously said, both contain, as suspended solids, polyelectrolyte and bacterial colonies deriving from the treatments undergone. These may have interacted with filter media, preventing them from performing the filtration. In particular, two types of interaction have been hypothesized: one of a physical nature, in which suspended solids have occluded some of the pores of materials, and one of a chemical type, i.e. polyelectrolyte and bacterial colonies, once at room temperature, have started again to react with the compounds present in the water, by using some of these compounds and producing others.

As for phosphorus, BC700, BC500 and AC were used for its felling. Figure 28 compares the best obtained results. Both biochars made P decrease in both waters. In contrast, activated carbon had no effect on wastewater "Chiaro Centrifughe", and led to a minimal decrease in wastewater "Chiaro Flottatori".

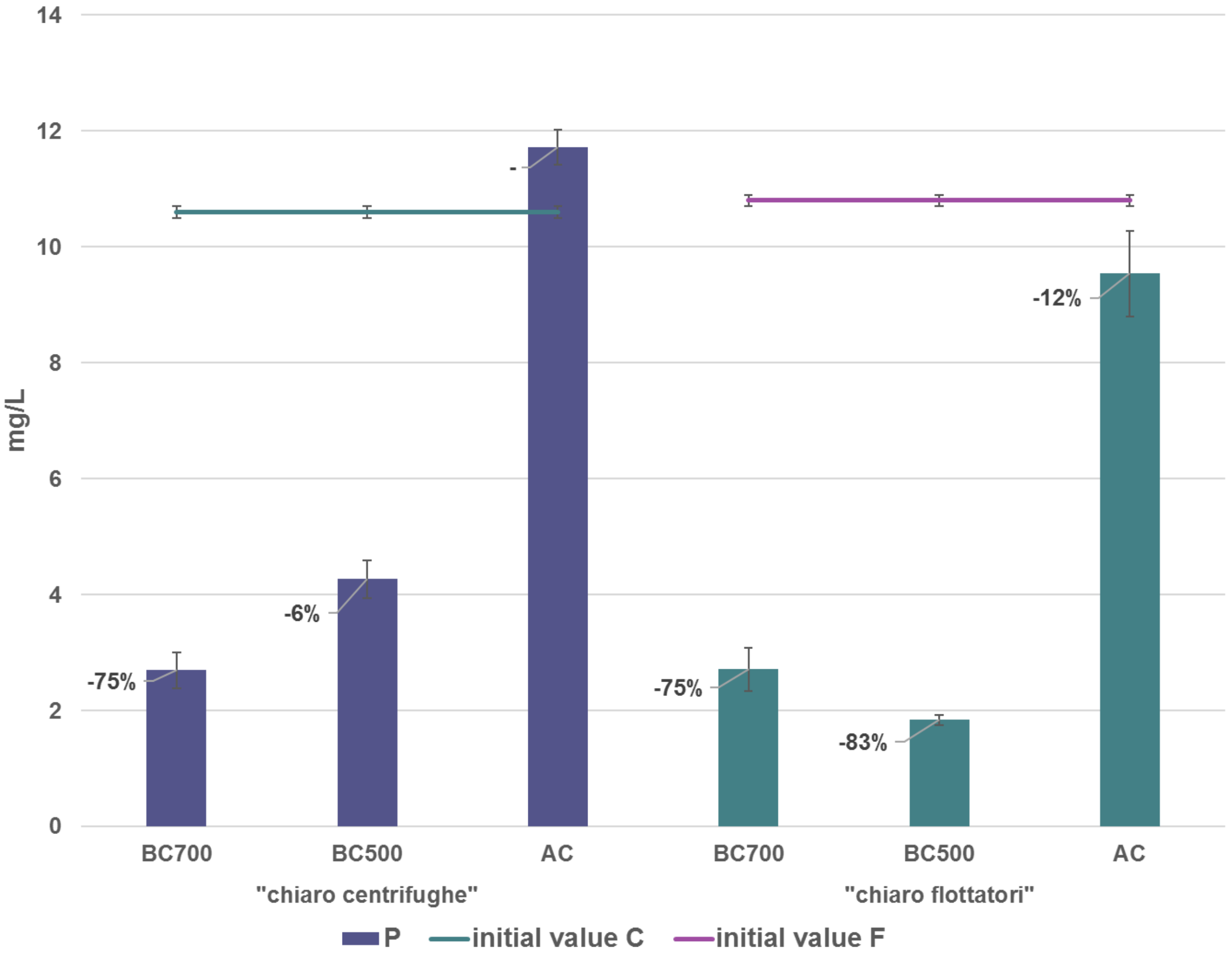


Figure 28 - Comparison in $PO_4^{3-}$ - P removal performance between AC, BC700, BC500 and Zeolite and with the initial value (best cases).

As discussed in section 3.3, the economic performances of biochars and AC were evaluated analysing their COD sorption capacity and their commercial prices. The result is that biochar economic performances are better than those of activated carbon: the biochar price per kg of COD removed from wastewater is found to be between 20 and 37 USD/kgCOD for biochar, while the price for activated carbon was between 58 and 245 USD/kgCOD.

For Phosphorus the price of biochar and activated carbon expressed as USD/kgP are much higher, due to the smaller reduction rate. In particular they are respectively 584 USD/kgP for BC700 and 3,659 USD/kgP for activated carbon.

The use of BC700 before purifying and disposing of wastewater would save a total of $1.37 \times 10^8$ €/year to Caviro EXTRA, net of the cost for the purchase of biochar. Furthermore, the sale of biochar, used as a filter, as fertilizer or as soil improver for agriculture would represent an additional income for the company.

# 5 Conclusions

In this thesis work, biochar was produced with an innovative technology, known as Thermo-Chemical Reforming (TCR®). The TCR® technology combines intermediate pyrolysis with a post-reforming phase, which increases and enhances the characteristics of the products: oil, biochar and syngas. For this work a laboratory plant was used, called TCR®2, which processes up to 2 kg of feedstock per hour.

Two types of biochar were produced, which differ from each other in the temperature of the post reformer. The first biochar was produced with a post-reformer temperature of 700°C (BC700), the second with a temperature of 500°C (BC500). From the characterization of the two biochars, a fundamental difference emerged for the BET surface. The BET of BC700 was 446 $m^2$/g, while the BET of BC500 was 286 $m^2$/g. This is reflected in significant differences in the performance of the two biochars used as filtering material. This difference in SSA was expected since, as said in the introduction, the TCR® technology allows to influence the surface of the biochar by modifying the time residence and increasing the temperature during the reforming step.

In the sorption tests, biochar has proved effective particularly in the abatement of COD. In particular, the BC700 reduced the COD up to about 50%, with a contact time of 6 hours in the water "Chiaro Centrifughe", and up to 30% in water "Chiaro Flottatori" for contact times greater than or equal to 6 hours. For all contact times, biochar has reduced COD by at least 10%.

The ability of biochar to reduce the COD content of wastewater has been compared with commercial materials, such as activated carbon and zeolites. The BC700 biochar performed better than all other filter media with both waters.

Regarding $NH_4$ and Cl, none of the filtering materials used in the experiment was able to decrease their concentration in both wastewaters. Cl removal is very complex with filter materials, so it will be necessary to investigate other methods. As for $NH_4$, the interactions with the solid material probably prevented its absorption, so the experiment will have to be repeated with an initial pre-treatment of the wastewater.

Finally, biochar has shown, unlike activated carbon and zeolites, to be a precious material for the pre-treatment of wastewater before its disposal, significantly lowering costs. Furthermore, the sale of the used biochar as a fertilizer could be an additional source of income for the company.

Future developments are listed in the following.

- It would be useful to evaluate the phosphorus reduction capacity of biochar by creating synthetic water in laboratory with known concentrations of phosphorus. In this way it will be possible to exclusively evaluate the biochar performance, avoiding interactions. Furthermore, it would be necessary to maintain the pH of the solution stable. To do so HCl can be added, since the pH tend to increase, paying attention that the amount of chlorine does not interfere with the phosphorus measurement methods.
- Although the results obtained, in particular regarding the COD, were satisfactory, it will be interesting to evaluate other methods of "water purification". One method could be to filter, with a 0.45 µm filter, the entire sample of wastewater before any type of analysis. This will prevent bacterial colonies and polyelectrolytes from resuming their activities, making the data difficult to interpret. Another method is to work with one or more filter columns. However, it is important that the amount of biochar and its granulometry are such that all solids are removed in the first section of the column (or in the first column) and that, in the next phase, the effective reduction of COD, $PO_4^{3-}$ and $NH_4^+$ etc takes place.

# 6 REFERENCES

Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., … Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere*, *99*, 19–33. https://doi.org/10.1016/j.chemosphere.2013.10.071

Alhashimi, H. A., & Aktas, C. B. (2017). Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis. *Resources, Conservation and Recycling*. https://doi.org/10.1016/j.resconrec.2016.11.016

Alling, V., Hale, S. E., Martinsen, V., Mulder, J., Smebye, A., Breedveld, G. D., & Cornelissen, G. (2014). The role of biochar in retaining nutrients in amended tropical soils. *Journal of Plant Nutrition and Soil Science*, *177*(5), 671–680. https://doi.org/10.1002/jpln.201400109

Barber, S. T., Yin, J., Draper, K., & Trabold, T. A. (2018a). Closing nutrient cycles with biochar- from filtration to fertilizer. *Journal of Cleaner Production*, *197*, 1597–1606. https://doi.org/10.1016/j.jclepro.2018.06.136

Barber, S. T., Yin, J., Draper, K., & Trabold, T. A. (2018b). Closing nutrient cycles with biochar- from filtration to fertilizer. *Journal of Cleaner Production*, *197*, 1597–1606. https://doi.org/10.1016/j.jclepro.2018.06.136

Blaszczak, R. (1999). *CATC Technical Bulletin: Choosing an adsorption system for VOC: carbon, zeolite or polymers? EPA-456/F-99-004.* Retrieved from http://www.epa.gov/ttn/catc

Bolzonella, D., Papa, M., Ros, C. Da, Muthukumar, L. A., & Rosso, D. (2019). Winery wastewater treatment : a critical overview of advanced biological processes. *Critical Reviews in Biotechnology*, *0*(0), 1–19. https://doi.org/10.1080/07388551.2019.1573799

Brito, A. G., Peixoto, J., Oliveira, J. M., Oliveira, J. A., Costa, C., Nogueira, R., & Rodrigues, A. (2007). Brewery and Winery Wastewater Treatment: Some Focal Points of Design and Operation. *Utilization of By-Products and Treatment of Waste in the Food Industry*, (May 2014), 1–316. https://doi.org/10.1007/978-0-387-35766-9

Carey, D. E., McNamara, P. J., & Zitomer, D. H. (2015). Biochar from Pyrolysis of Biosolids for Nutrient Adsorption and Turfgrass Cultivation. *Water Environment Research*, *87*(12), 2098–2106. https://doi.org/10.2175/106143015x14362865227391

Chen, B., Zhou, D., & Zhu, L. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science and Technology*, *42*(14), 5137–5143. https://doi.org/10.1021/es8002684

Conti, R., Jäger, N., Neumann, J., Apfelbacher, A., Daschner, R., & Hornung, A. (2017a). Thermocatalytic Reforming of Biomass Waste Streams. *Energy Technology*, *5*(1), 104–110. https://doi.org/10.1002/ente.201600168

Conti, R., Jäger, N., Neumann, J., Apfelbacher, A., Daschner, R., & Hornung, A. (2017b). Thermocatalytic Reforming of Biomass Waste Streams. *Energy Technology*, *5*(1), 104–110. https://doi.org/10.1002/ente.201600168

Day, P., Cribb, J., Boland, A.-M., Shanahan, M., Oemcke, D., Kumar, A., … Burgi, A. (2011). Winery Wastewater Management & Recycling Operational Guidelines. *Grape and Wine Research and Development Corporation GWRDC Project Manager: Troy Fischer*.

Ercoli, L., Bonari, E., & Produttiva, L. a F. (2017). Acque reflue derivanti da macelli aziendali. Retrieved from https://www.iris.sssup.it/retrieve/handle/11382/303521/944/capitolo5copia.pdf

Fagerlund, G. (1973). Determination of specific surface by the BET method. *Matériaux et Construction*, *6*(3), 239–245. https://doi.org/10.1007/BF02479039

Galinato, S. P., Yoder, J. K., & Granatstein, D. (2011). The economic value of biochar in crop production and carbon sequestration. *Energy Policy*, *39*(10), 6344–6350. https://doi.org/10.1016/j.enpol.2011.07.035

Garcia, K., Loewen, T., Oland, J., Garn, J., & Britain, A. (2018). *Winery Process Wastewater Management Handbook : Best Practices and Technologies*.

Hagemann, N., Spokas, K., Schmidt, H. P., Kägi, R., Böhler, M. A., & Bucheli, T. D. (2018). Activated carbon, biochar and charcoal: Linkages and synergies across pyrogenic carbon's ABCs. *Water (Switzerland)*, *10*(2), 1–19. https://doi.org/10.3390/w10020182

Hornung, A. (2014). *Transformation of Biomass: Theory to Practice*. *Transformation of Biomass: Theory to Practice*. https://doi.org/10.1002/9781118693643

Huggins, T. M., Haeger, A., Biffinger, J. C., & Ren, Z. J. (2016). Granular biochar compared with activated carbon for wastewater treatment and resource recovery. *Water Research*, *94*, 225–232. https://doi.org/10.1016/j.watres.2016.02.059

Hussain, M., Farooq, M., Nawaz, A., Al-Sadi, A. M., Solaiman, Z. M., Alghamdi, S. S., … Siddique, K. H. M. (2017). *Biochar for crop production: potential benefits and risks*. *Journal of Soils and Sediments* (Vol. 17). Journal of Soils and Sediments. https://doi.org/10.1007/s11368-016-1360-2

Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., & Cao, X. (2012). Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Bioresource Technology*, *110*, 50–56. https://doi.org/10.1016/j.biortech.2012.01.072

Jäger, N., Conti, R., Neumann, J., Apfelbacher, A., Daschner, R., Binder, S., & Hornung, A. (2016). Thermo-Catalytic Reforming of Woody Biomass. *Energy and Fuels*, *30*(10), 7923–7929. https://doi.org/10.1021/acs.energyfuels.6b00911

Jain, A., Balasubramanian, R., & Srinivasan, M. P. (2016). Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review. *Chemical Engineering Journal*, *283*, 789–805. https://doi.org/10.1016/j.cej.2015.08.014

Kim, K. C., Yoon, T. U., & Bae, Y. S. (2016). Applicability of using CO2 adsorption isotherms to determine BET surface areas of microporous materials. *Microporous and Mesoporous Materials*, *224*, 294–301. https://doi.org/10.1016/j.micromeso.2016.01.003

Kim, P., Hensley, D., & Labbé, N. (2014). Nutrient release from switchgrass-derived biochar pellets embedded with fertilizers. *Geoderma*, *232–234*, 341–351. https://doi.org/10.1016/j.geoderma.2014.05.017

Manyuchi, M. M., Mbohwa, C., & Muzenda, E. (2018). Potential to use municipal waste bio char in wastewater treatment for nutrients recovery. *Physics and Chemistry of the Earth*, *107*(July), 92–95. https://doi.org/10.1016/j.pce.2018.07.002

Neumann, J., Binder, S., Apfelbacher, A., Gasson, J. R., Ramírez García, P., & Hornung, A. (2015). Production and characterization of a new quality pyrolysis oil, char and syngas from digestate - Introducing the thermo-catalytic reforming process. *Journal of*

*Analytical and Applied Pyrolysis*, *113*, 137–142. https://doi.org/10.1016/j.jaap.2014.11.022

Neumann, J., Jäger, N., Apfelbacher, A., Daschner, R., Binder, S., & Hornung, A. (2016). Upgraded biofuel from residue biomass by Thermo-Catalytic Reforming and hydrodeoxygenation. *Biomass and Bioenergy*, *89*, 91–97. https://doi.org/10.1016/j.biombioe.2016.03.002

Novais, S. V., Zenero, M. D. O., Barreto, M. S. C., Montes, C. R., & Cerri, C. E. P. (2018). Phosphorus removal from eutrophic water using modified biochar. *Science of the Total Environment*, *633*, 825–835. https://doi.org/10.1016/j.scitotenv.2018.03.246

Oliveira, F. R., Patel, A. K., Jaisi, D. P., Adhikari, S., Lu, H., & Khanal, S. K. (2017, December 1). Environmental application of biochar: Current status and perspectives. *Bioresource Technology*. Elsevier Ltd. https://doi.org/10.1016/j.biortech.2017.08.122

Ouadi, M., Jaeger, N., Greenhalf, C., Santos, J., Conti, R., & Hornung, A. (2017). Thermo-Catalytic Reforming of municipal solid waste. *Waste Management*. https://doi.org/10.1016/j.wasman.2017.06.044

Paneque, M., De la Rosa, J. M., Franco-Navarro, J. D., Colmenero-Flores, J. M., & Knicker, H. (2016). Effect of biochar amendment on morphology, productivity and water relations of sunflower plants under non-irrigation conditions. *Catena*, *147*, 280–287. https://doi.org/10.1016/j.catena.2016.07.037

Pellera, F. M., Giannis, A., Kalderis, D., Anastasiadou, K., Stegmann, R., Wang, J. Y., & Gidarakos, E. (2012). Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products. *Journal of Environmental Management*, *96*(1), 35–42. https://doi.org/10.1016/j.jenvman.2011.10.010

Petrović, J. T., Stojanović, M. D., Milojković, J. V., Petrović, M. S., Šoštarić, T. D., Laušević, M. D., & Mihajlović, M. L. (2016). Alkali modified hydrochar of grape pomace as a perspective adsorbent of Pb2+ from aqueous solution. *Journal of Environmental Management*, *182*, 292–300. https://doi.org/10.1016/j.jenvman.2016.07.081

Rajapaksha, A. U., Chen, S. S., Tsang, D. C. W., Zhang, M., Vithanage, M., Mandal, S., … Ok, Y. S. (2016, April 1). Engineered/designer biochar for contaminant removal/immobilization from soil and water: Potential and implication of biochar modification. *Chemosphere*. Elsevier Ltd. https://doi.org/10.1016/j.chemosphere.2016.01.043

Regmi, P., Garcia Moscoso, J. L., Kumar, S., Cao, X., Mao, J., & Schafran, G. (2012). Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process. *Journal of Environmental Management*, *109*, 61–69. https://doi.org/10.1016/j.jenvman.2012.04.047

Rillig, M. C., Wagner, M., Salem, M., Antunes, P. M., George, C., Ramke, H. G., … Antonietti, M. (2010). Material derived from hydrothermal carbonization: Effects on plant growth and arbuscular mycorrhiza. *Applied Soil Ecology*, *45*(3), 238–242. https://doi.org/10.1016/j.apsoil.2010.04.011

Rodríguez-Reinoso, F., & Marsh, H. (1992). *Activated Carbon (Activation Processes)*. *Activated Carbon*.

Schmidt, H. P., Kammann, C., Niggli, C., Evangelou, M. W. H., Mackie, K. A., & Abiven, S. (2014). Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality. *Agriculture, Ecosystems and Environment*, *191*, 117–123. https://doi.org/10.1016/j.agee.2014.04.001

Schmitt, N., Apfelbacher, A., Jäger, N., Daschner, R., Stenzel, F., & Hornung, A. (2019). Thermo-chemical conversion of biomass and upgrading to biofuel: The Thermo-Catalytic Reforming process – A review. *Biofuels, Bioproducts and Biorefining*, *13*(3), 822–837. https://doi.org/10.1002/bbb.1980

Shackley, S., Ruysschaert, G., & Glaser, B. (2016). *Biochar in European soils and agriculture: Science and practice*. *Biochar in European Soils and Agriculture: Science and Practice*. https://doi.org/10.4324/9781315884462

Sizmur, T., Fresno, T., Akgül, G., Frost, H., & Moreno-Jiménez, E. (2017, December 1). Biochar modification to enhance sorption of inorganics from water. *Bioresource Technology*. Elsevier Ltd. https://doi.org/10.1016/j.biortech.2017.07.082

Sluiter, J. B., Ruiz, R. O., Scarlata, C. J., Sluiter, A. D., & Templeton, D. W. (2010). *Compositional analysis of lignocellulosic feedstocks. 1. Review and description of methods. Journal of agricultural and food chemistry* (Vol. 58).

https://doi.org/10.1021/jf1008023

Song, Y., Li, Y., Cai, Y., Fu, S., Luo, Y., Wang, H., … Chang, S. X. (2019). Biochar decreases soil N 2 O emissions in Moso bamboo plantations through decreasing labile N concentrations, N-cycling enzyme activities and nitrification/denitrification rates. *Geoderma*, *348*(January), 135–145. https://doi.org/10.1016/j.geoderma.2019.04.025

Stenzel, F., Heberlein, M., Klinner, T., & Hornung, A. (2016). Production of activated carbon from agricultural residues. *International Journal of ChemTech Research*, *9*(8), 62–69.

Stratful, I., Scrimshaw, M. D., & Lester, J. N. (2001). Conditions influencing the precipitation of magnesium ammonium phosphate. *Water Research*, *35*(17), 4191–4199. https://doi.org/10.1016/S0043-1354(01)00143-9

Sun, Y., Qi, S., Zheng, F., Huang, L., Pan, J., Jiang, Y., … Xiao, L. (2018). Organics removal, nitrogen removal and N2O emission in subsurface wastewater infiltration systems amended with/without biochar and sludge. *Bioresource Technology*, *249*(August 2017), 57–61. https://doi.org/10.1016/j.biortech.2017.10.004

Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., & Yang, Z. (2015, April 1). Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*. Elsevier Ltd. https://doi.org/10.1016/j.chemosphere.2014.12.058

Tong, X. J., Li, J. Y., Yuan, J. H., & Xu, R. K. (2011). Adsorption of Cu(II) by biochars generated from three crop straws. *Chemical Engineering Journal*, *172*(2–3), 828–834. https://doi.org/10.1016/j.cej.2011.06.069

Trakal, L., Šigut, R., Šillerová, H., Faturíková, D., & Komárek, M. (2014). Copper removal from aqueous solution using biochar: Effect of chemical activation. *Arabian Journal of Chemistry*, *7*(1), 43–52. https://doi.org/10.1016/j.arabjc.2013.08.001

Yanmei, Z., Bin, G., Zimmerman, A. R., Fang, J., Sun, Y., & Cao, X. (2013). Sorption of heavy metals on chitosan-modified biochars and its biological effects. *Chemical Engineering Journal*, *231*, 512–518.

Yi, M., & Chen, Y. (2018). Enhanced phosphate adsorption on Ca-Mg-loaded biochar derived from tobacco stems. *Water Science and Technology*, *78*(11), 2427–2436. https://doi.org/10.2166/wst.2019.001

Zhang, W., Wang, L., & Sun, H. (2011). Modifications of black carbons and their influence on pyrene sorption. *Chemosphere*, *85*(8), 1306–1311. https://doi.org/10.1016/j.chemosphere.2011.07.042

# ACKNOWLEDGMENTS

I wish to thank my supervisors at Fraunhofer UMSICHT Institute, Dr. Fabian Stenzel and Dr. Juan Pablo Gutierrez, who guided me through this thesis work.

I would also like to thank professor Andrea Contin, to whom I am indebted for his continuous mentoring, encouragement, and support.

A million thanks to Nicolas, supervisor and friend, who always brings me back down to earth and helps me see things from the best perspective. Thanks for having my back.

Thanks to Diego, Stefano e Denis, whose doors were always open whenever I ran into a trouble spot or had a question about my research or writing.

My appreciation extends to all the other EMRG members, for having welcomed me into the group two years ago and making me feel appreciated every moment.

I wish to thank also professor Enrico Dinelli, for having been a guide constantly present in these five years, from the very first moment.

My deepest gratitude goes to my colleagues and friends at Fraunhofer UMSICHT Anna, Fjolle, Zairah, Cesar, Frank, Galih and Shashank, for their assistance, help, cooperation and friendship.

And to my Italian friends and relatives Roberta, Tommaso, Davide and Luca, for being by my side even from far away.

Thanks to my boyfriend, for being patient while I was struggling in Germany during my internship, and for supporting me all the time (and for providing me with movies and TV series).

I must express my very profound gratitude to my parents for all they did for me and they gave me. This accomplishment would not have been possible without them. Thank you. I love you.

Finally, my thoughts to my poor Climate KIC friends. Good luck finding the exit door of this maze we have been in for the past two years!

Thank you all so much.